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COMMITTEE ON PAPERS AND PUBLICATIONS.

## CONTENTS.

PAGE.

On the Behavior of Allylmalonic, Allylacetic, and Ethylidenepropionic Acids when Boiled with Caustic Soda Solutions. By John G. Spenzer ..... 1

The Phosphomolybdic Acid Test as Applied to Lard Analysis. By George F. Tennille ..... 33

Some New Solvents for Perchromic Acid. By William M. Grosvenor, Jr ..... 41

Some Facts Observed in the Determination of Phosphoric Acid by the Molybdic Acid Process. By Rudolf de Roode ..... 43

The Addition of Calcium Chloride to the Solution of a Fertilizer in the Determination of Potash. By Rudolf de Roode ..... 46

On the Preparation of Ammonium Citrate Solution. By Rudolf de Roode ..... 47

The Determination of Potash in Manures. By W. E. Garrigues ..... 47

The Rapid and Accurate Analysis of Bone-black. By W. D. Horne, 51

The Asphalt Question. By S. F. Peckham ..... 55

Quick Estimation of Starch. By P. L. Hibbard ..... 64

Alkali and Sulphurous Acid Processes Used in the Manufacture of Starch from Corn. By Horace E. Horton ..... 68

NEW BOOKS: A Text-Book of Volumetric Analysis, with Special Reference to the Volumetric Processes of the Pharmacopeia of the United States; A Text-Book of Inorganic Chemistry; Die Maschinellen Hilfsmittel der chemischen Technik; The Elementary Nature of Chlorine ..... 69

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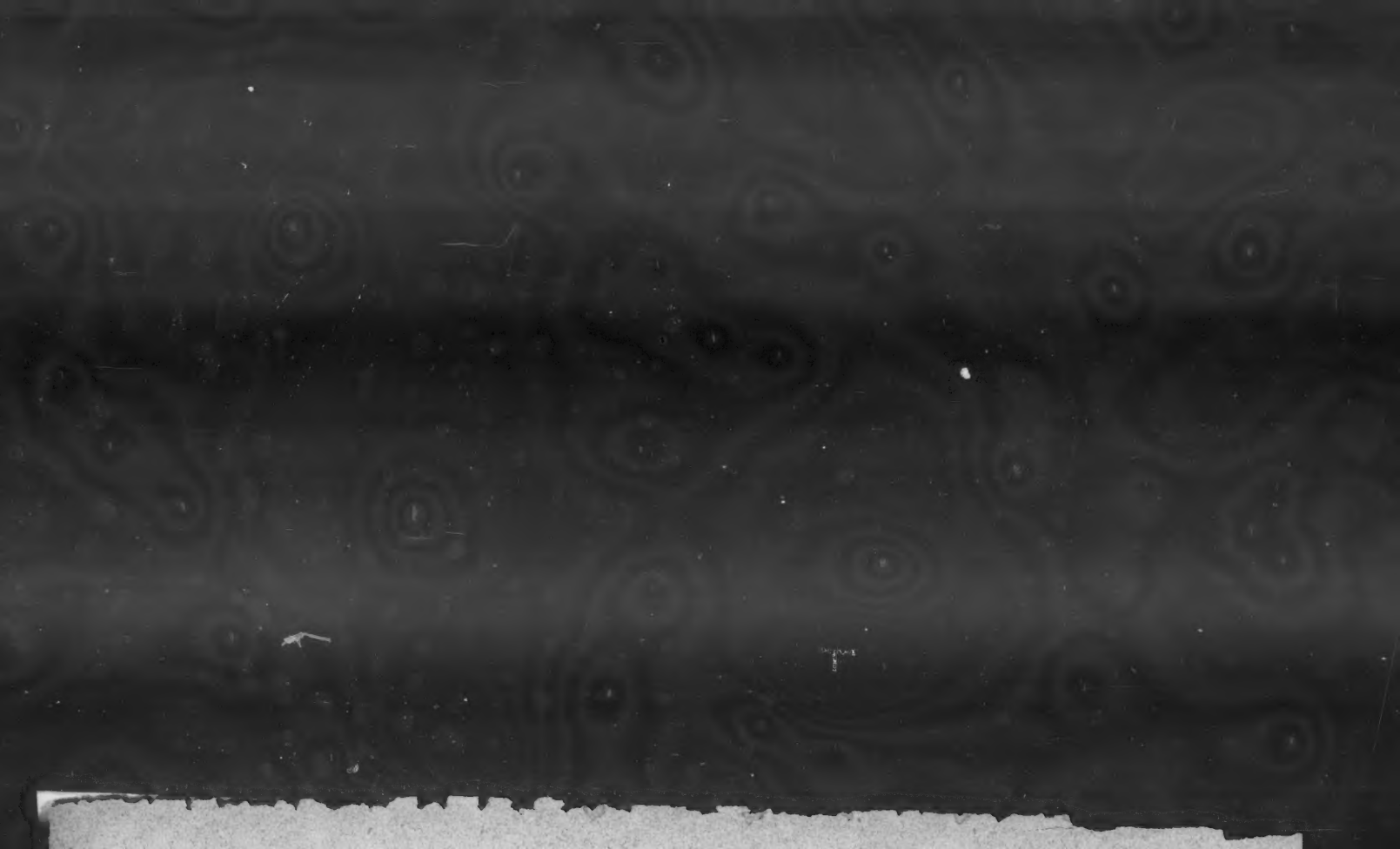
PAPERS ACCEPTED FOR PUBLICATION:

The Determination of Potash in Kainite. By Rudolf de Roode.

The Oxidation of Organic Matter and the Decomposition of Ammonium Salts by Aqua Regia in lieu of Ignition, in the Determination of Potash in Fertilizers. By Rudolf de Roode.

On Certain Phenomena Observed in the Precipitation of Antimony from Solutions of Potassium Antimonyl Tartrate. By J. H. Long.



Issued with January Number, 1895.

# Proceedings.

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Brown, W. G., Division of Chemistry, Department of Agriculture, Washington, D. C.

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Hewitt, Edward R., Room 8, East 9th St., New York City.

Mumper, W. N., 228 West State St., Trenton, N. J.

Waterman, C. N., 345 Decatur St., Brooklyn, N. Y.

Weems, J. B., Experiment Station, Geneva, N. Y.

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## MEETINGS OF THE SECTIONS.

### NEW YORK SECTION.

Friday Evening, Dec. 14, 1894.

Prof. P. T. Austen, presiding.

Forty members present.

Dr. Thomas B. Osborne, of New Haven, read a paper on the Chemical Nature of Diastase, showing that by successive treatment with ammonium sulphate, solution in water, dialysis into alcohol, and extraction with sodium chloride solution, a nitrogenous substance can be prepared from malt extract which has an enormous diastatic power, and that by this means pure diastase may be isolated.

Dr. Bartley presented facts to prove the injurious effects of

glucose upon the digestion, and commented upon the probable reasons therefor.

Prof. Austen presented an essay upon careless diction in chemical text-books.

## WASHINGTON SECTION.

Nov. 8, 1894.

President W. H. Seaman in the chair.

Ten members present.

The resignation of Prof. J. C. Gorden was read and accepted.

A letter from John W. Hoyt was read, asking the co-operation of the Society in the formation of a National Post-Graduate University. The President of the Society was asked to assure Mr. Hoyt of the sympathy and co-operation of the Society.

H. W. Wiley reported as to the First Congress of Chemists at the San Francisco Exposition, and referred to the probable formation of a Local Section of the American Chemical Society on the Pacific Coast.

A paper was read by W. D. Bigelow on the "Coloring Matter in California Red Wines." This was a preliminary notice of work, not yet completed, which will later be made the subject of a more extended communication. He had subjected samples of ninety-four varieties of California red wines to the same examination as that commonly applied for the coloring matter in European wines. "According to the reactions obtained with these reagents, the coloring matter of California wines appears to be much more uniform than that of European wines. Sometimes, however, a gray, or yellowish, or orange-gray precipitate or solution is obtained with reagents which are said to give a green or grayish-green with French wines. On the other hand, no reactions were obtained which are said to be characteristic of wines colored with vegetable pigments."

### *Discussion.*

Dr. Wiley said that the inducements for adulteration of California wines were not great on account of their low price. The difficulties in distinguishing between a natural and a spurious

article became very great at a point where the results of analyses might just as readily be interpreted one way as another, and to obtain greater certainty beyond this point the work was undertaken in the laboratory of the Agricultural Department.

Mr. Bigelow, in response to the question as to the success of the use of the spectroscope in the examination of wines, said that it had been employed with some success in the detection of cochineal and of the coal-tar colors, but for the detection of vegetable colors it was unsatisfactory, owing to the fact, no doubt, that they were so closely allied to the natural colors of the wine.

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AMERICAN CHEMICAL SOCIETY.

## ON THE BEHAVIOR OF ALLYLMALONIC, ALLYLACETIC, AND ETHYLIDENEPROPIONIC ACIDS WHEN BOILED WITH CAUSTIC SODA SOLUTIONS.

### CONTRIBUTIONS TO THE KNOWLEDGE OF PROPYLIDENEACETIC ACID.[1]

BY JOHN G. SPENZER.

Received October 26, 1894.

DURING the preparation of hydropiperic acid, Fittig and Buri,[2] in 1883, discovered that in the reduction of piperic acid by means of sodium amalgam, two very different isomeric hydropiperic acids were formed, according as the reducing fluid was kept almost neutral, or allowed to become strongly alkaline by not adding acid. In the first procedure they obtained the already known and now designated $\alpha$ hydropiperic acid, while in the second process together with the $\alpha$ acid, larger or smaller quantities of the new isomeric $\beta$ hydropiperic acid appeared, which seemed to have been produced from the $\alpha$ acid through the agency of the caustic soda formed in the reducing fluid.

In fact it was proven experimentally, by heating the $\alpha$ hydropiperic acid, with caustic soda on the water-bath, that $\beta$ hydropiperic acid could be obtained.

Weinstein[3] and Regel[4] were induced by Fittig to examine the two isomeric acids further, and because of its behavior on substituting bromine and hydrobromic acid as also in the oxidation with potassium permanganate they came to the interesting con-

[1] Read before Section C., American Association for Advancement of Science, Brooklyn, N. Y., August 20, 1894.

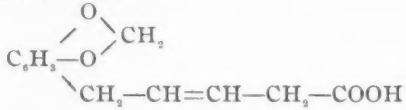
[2] *Ann. Chem.*, **216**, 171.

[3] Ibid, **227**, 31.

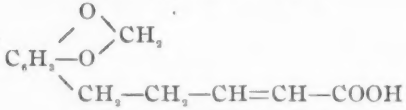
[4] *Ber. d. Chem. Ges.*, **20**, 414.

clusion that the $\alpha$ hydropiperic acid was a $\beta\,\gamma$ unsaturated acid, and that the $\beta$ hydropiperic acid must be an $\alpha\,\beta$ unsaturated acid.

Therefore, by the conversion of the $\alpha$ hydropiperic acid into the $\beta$ hydropiperic acid, under the influence of hot caustic soda, a moving of the double bond of union towards the carboxyl group takes place as follows:

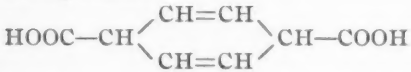


$\alpha$ hydropiperic acid ($\beta\,\gamma$)

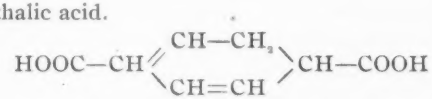


$\beta$ hydropiperic acid ($\alpha\,\beta$)

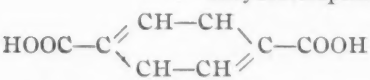
Other such displacements of the double bonds of union through the agency of alkalies and even by boiling water were soon found. Baeyer[1] observed, that the $\delta^{2,5}$ dihydroterephthalic acid, became the $\delta^{1,5}$ dihydroterephthalic acid, when boiled with water, and the latter, in turn, when boiled with caustic soda, produced the $\delta^{1,4}$ dihydroterephthalic acid, according to the following scheme:



$\delta^{2,5}$ dihydroterephthalic acid.



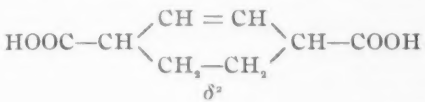
$\delta^{1,5}$ dihydroterephthalic acid.



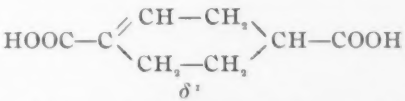
$\delta^{1,4}$ dihydroterephthalic acid.

Further $\delta^{2}$ tetrahydroterephthalic acid when treated with hot caustic soda produces $\delta^{1}$ tetrahydroterephthalic acid as follows:

[1] *Ann. Chem.*, 251, 257.



$\delta^2$



$\delta^1$

Finally hydromuconic acid according to Baeyer and Rupe[1] by the same treatment is changed into an isomeric $\alpha\ \beta$ acid, as:

$HOOC—CH_2—CH=CH—CH_2—COOH$

$\beta\ \gamma$ hydromuconic acid.

$HOOC—CH_2—CH_2—CH=CH—COOH$

$\alpha\ \beta$ hydromuconic acid.

Even previous to this Fittig[2] had been led to the conclusion, that in the potassa-fusion of hydrosorbic acid a moving of the double union from the $\beta\ \gamma$ to the $\alpha\ \beta$ position must also take place, since the splitting, thereby occasioned, occurs at the $\alpha\ \beta$ position with the production of butyric and acetic acids, still the hydrosorbic acid is unquestionably a $\beta\ \gamma$ unsaturated acid, which, therefore, must split into two molecules of propionic acid.

All these observations but favored the belief, that the shoving of the double union in the unsaturated acids towards the carboxyl group when boiled with caustic soda was a general one.

To prove the correctness of this point, Fittig began with his pupils, on a series of $\beta\ \gamma$ unsaturated acids, and in all the researches as yet made, no exception has been found. Of the aromatic acids, aside from hydropiperic acid the following have been examined:

Phenyl $\beta\ \gamma$ pentinic acid, which gives, according to T. Hoffmann, with boiling caustic soda, the isomeric phenyl $\alpha\ \beta$ pentinic acid.

$C_6H_5—CH_2—CH=CH—CH_2—COOH$

$\beta\ \gamma$

$C_6H_5—CH_2—CH_2—CH=CH—COOH$

$\alpha\ \beta$

[1] Ibid, 256, 1. [2] Ibid, 255, 13.

Phenylisocrotonic acid is changed, after Luib, by a like treatment into benzylacrylic acid.

$$C_6H_5-CH=CH-CH_2-COOH$$
$$\beta\ \gamma$$

$$C_6H_5-CH_2-CH=CH-COOH$$
$$\alpha\ \beta$$

In the "fatty series" this change takes place regularly. Baker obtained from hydrosorbic acid by boiling with caustic soda $\beta$ propylacrylic acid.

$$CH_3-CH_2-CH=CH-CH_2-COOH$$
$$\beta\ \gamma$$

$$CH_3-CH_2-CH_2=CH-COOH$$
$$\alpha\ \beta$$

Feurer, from isoheptylic obtained isobutylacrylic acid.

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\diagdown\!\!\diagup CH-CH=CH-CH_2-COOH$$
$$\beta\ \gamma$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\diagdown\!\!\diagup CH-CH_2-CH=CH-COOH$$
$$\alpha\ \beta$$

Weill, from $\beta,\gamma$ isoctylic the $\alpha\ \beta$ isoamylacrylic acid.

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\diagdown\!\!\diagup CH-CH_2-CH=CH-CH_2-COOH$$
$$\beta\ \gamma$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!\diagdown\!\!\diagup CH-CH_2-CH_2-CH=CH=COOH$$
$$\alpha\ \beta$$

The present work was taken up with a view of extending these researches by including acids of the "$\gamma\ \delta$ series."

The supposition of Zincke and Kuester[1] that the $\gamma\ \delta$ unsaturated acids would, when boiled with caustic soda, also allow of a displacement of their double bonds, can be given as one of the principal reasons for beginning the investigations.

If the supposition of Zincke and Kuester is correct, then the following, which they looked upon as very probable, would

[1] *Ber. d. chem. Ges.*, **24**, 909.

have been most interesting: that is, if the $\gamma\ \delta$ acids should suffer their double bond to be moved, then it would be an easy matter to produce a $\beta\ \gamma$ and in turn an $\alpha\ \beta$ acid, for example, from allylacetic acid, ethylidenepropionic acid, and finally propylideneacetic acid should be obtained by boiling with caustic soda, according to the following:

$$\underset{\beta\ \delta}{CH_2=CH-CH_2-CH_2-COOH} \rightarrow \underset{\beta\ \gamma}{CH_3-CH=CH-CH_2-COOH} \rightarrow \underset{\alpha\ \beta}{CH_3-CH_2-CH=CH-COOH}$$

The first part of this paper is taken up in the description of the results of the experiments, on two $\gamma\ \delta$ acids, allylmalonic and allylacetic acids.

In the case of both of these acids, the following surprising results were obtained. On boiling with caustic soda no conversion into the corresponding $\beta\ \gamma$ and $\alpha\ \beta$ unsaturated acids could be detected. This passive behavior, of both of these representatives of the "$\gamma\ \delta$ series," is, therefore, the more remarkable, since from analogy, taken from the already observed inclination of terminal methylene radicals, to form methyl groups, as for instance, Faworsky[1] found in the unsaturated hydrocarbons, a complete change might be expected here. On the other hand Baeyer[2] has verified these exceptions to Faworsky's rule in the case of the hydrated phthalic acids.

Finally, if this difference to boiling caustic soda should be asserted in other $\gamma\ \delta$ acids and become a general characteristic of this series, then through this means a sharp and decided distinguishing property has been discovered between the $\gamma\ \delta$ and the $\beta\ \gamma$ unsaturated acids, which, moreover, behave alike in the substitution of hydrobromic acid and the decomposition of the product, by means of water and alkalies (Messerschmidt[3]); as also in the substitution of bromine (Urban[4]); and in the treatment with potassium permanganate (Urban[5]).

The second part of this research is given to a description of the

[1] J. *prakt. Chem.*, 44, 212. [2] *Ann. Chem.*, 269, 150. [3] Ibid, 208, 93.
[4] Ibid, 268, 60. [5] Ibid, 268, 32.

results obtained in the treating with caustic soda the $\beta\gamma$ acid corresponding to allylacetic acid, that is, ethylidenepropionic acid.

As a result it was found that this $\beta\gamma$ unsaturated acid, like all the others, which have as yet been investigated, on boiling with caustic soda, allowed the double union to be shoved to the $\alpha\beta$ position, with the formation of propylideneacetic acid, formerly known, but until now only in the impure state.

Even from the first, investigators on the moving of the double bond of union, through the influence of boiling caustic soda, busied themselves with efforts to explain the mechanism of the reaction.

Based on analogous reactions Weinstein[1] suggested that by warming the $\beta\gamma$ unsaturated acids with caustic soda the elements of water are taken up and an oxy acid formed, and this in turn, giving it up again, an $\alpha\beta$ unsaturated acid results, as follows:

1. $R-CH=CH-CH_2-COOH + H_2O =$
   $\beta\gamma$ unsaturated.
   $R-CH_2-CH(OH)-CH_2-COOH$
   $\beta$ oxy acid.

2. $R-CH-CH(OH)-CH-COOH - H_2O =$
   $R-CH_2-CH=CH-COOH$
   $\alpha\beta$ unsaturated.

This meanwhile purely hypothetical $\beta$ oxy acid, forms, therefore, the intermediate step between the two isomeric unsaturated acids.

Although Weinstein himself could not isolate this oxy acid still it has been formed repeatedly since then, thus:

Luib obtained from phenylisocrotonic acid phenyl $\beta$ oxybutyric acid $C_6H_5-CH_2-CH(OH)-CH_2-COOH$.

Hoffmann from phenyl $\beta\gamma$ pentinic acid produced phenyl $\beta$ oxyvalerianic acid.

$$C_6H_5-CH_2-CH_2-CH(OH)-CH_2-COOH.$$

However, just through Hoffmann's careful investigations, the idea that the $\beta$ oxy acid was the middle link, in the change

[1] *Ann. Chem.*, 227, 31.

from the $\beta\ \gamma$ unsaturated, to the $\alpha\ \beta$ acids was made somewhat doubtful.

He found for example that the $\beta\ \gamma$ acid after six hours boiling with caustic soda gave fifty per cent. of $\alpha\ \beta$ acid without any trace of $\beta$ oxy acid, and that further, the formation of the oxy acid required a very long and protracted treatment with the alkali, and that finally, the $\beta$ oxy acid can be most easily produced, by boiling the $\alpha\ \beta$ acid with caustic soda. Briefly, his observations leave the impression as if the $\beta$ oxy acid is not the intervening middle link between $\beta\ \gamma$ and $\alpha\ \beta$ acids, but is a secondary one to, and resulting from the $\alpha\ \beta$ acid.

In the "fatty series," on the contrary, the reaction seems to follow the course of the above scheme of Weinstein even if it has certain restrictions.

Baker's work pointed to, and Feurer's observations made it certain, that the three acids which he examined $\beta\ \gamma$ isoheptylic, $\beta$ oxydimethylvalerianic, and $\beta$ isobutylacrylic acids, when boiled with caustic soda, gave certain quantities of both of the others; the reaction does not, however, proceed smoothly in every sense of the term, but only to a certain limit, the $\beta$ oxy acid always forming the intermediate product of the two unsaturated isomers.

These observations also cover the results described in the second part of this paper, they having been also noticed in the examination of the $\beta$ oxy valerianic acid obtained from ethylidenepropionic acid.

PART I.

*On the behavior of allylmalonic and allylacetic acids when boiled with caustic soda solutions.*

PART II.

*On the behavior of ethylidenepropionic acid when boiled with caustic soda.*

*Contributions to the knowledge of propylideneacetic acid.*

## PART I.

*Preparation of Allylmalonic Acid.*—The allylmalonic acid was produced according to Conrad and Bischoff,[1] from malonic acid, ethyl ester, and allyl iodide.

[1] *Ann. Chem.*, 204, 168.

The malonic acid ethyl ester was obtained from Claisen and Crismer's[1] modification of Conrad's[2] method; the allyl iodide in turn was prepared after Kannonikoff and Saytzew[3] and Wagner's[4] improved suggestions of Berthelot and Luca.[5]

Since the purity of the allylmalonic acid depends principally on the absolute purity of the allyl iodide, a few precautionary hints, which have recommended themselves during the course of preparation, may not be amiss here.

1. Some ignited sand was put into the retort, thereby overcoming, on the one hand, the danger of breaking the latter through the phosphorus or iodine becoming attached to the bottom of the retort, and on the other, the action of the phosphorus is rendered more uniform and regular.

2. The retort was filled to one-half or at least one-third of its capacity.

3. It is particularly desirable that the phosphorus react directly as it is brought into the retort and that the allyl iodide distill over at once; this is facilitated by covering the upper part of the bowl and beak of the retort with a cloth to guard against cooling.

If the allyl iodide is not carried over as soon as formed, then much isopropyl iodide is produced, which is only with the greatest difficulty separated from the allyl iodide. Through repeated careful fractional distillations a preparation boiling between 99° and 102° C. and possessed of only a light-red color, was obtained.

To prepare the allylmalonic acid ester, the allyl iodide was run as rapidly as possible into the well-cooled sodium malonic acid ester and the product obtained after two hours boiling, separated by shaking with ice-water, and fractioning without further drying. The fractions were collected at every 5° from 150° to 200°, and at every 2° from 200° to 235° C.

After repeated and successive fractioning the four portions from 218° to 226° were taken to be pure and so used.

The saponification of the ester, which Conrad and Bischoff[6] performed with potassium hydroxide was in this case accomplished with barium hydroxide, in which the four fractions from

[1] Ibid., 218, 131. [2] Ibid., 204, 131. [3] *Ann. Chem.*, 185, 191.
[4] *Ber. d. chem. Ges.*, 9, 1810. [5] *Ann. Chem.*, 204, 168. [6] *Ann. Chem.*, 204, 168.

218° to 226° were separately treated. After the saponification was complete, the contents of the flask were diluted with hot water and the excess of barium hydroxide removed by means of carbonic acid gas; it was now filtered, and the filtrate evaporated to obtain the crystalline barium allylmalonate in fractions, the several crystallizations of the original fractions being held separate, until the subsequent decomposition by means of hydrochloric acid proved them to be pure.

Thanks, to this careful and protracted process of fractioning, a white, almost perfectly pure acid was obtained, from which through the aid of the acid barium salt, an absolutely pure acid melting at 105° C. was prepared. The production of pure acid amounted to thirty-three per cent. of the theory.

*Boiling Allylmalonic Acid with Caustic Soda Solution.*—Two experiments were performed.

In the first one, ten grams of pure allylmalonic acid were boiled for twenty hours (in a copper flask connected with a return condenser) with ten times the amount of caustic soda necessary for neutralization in a ten per cent. aqueous solution. Allowed to cool, the alkaline liquid was strongly acidified with sulphuric acid and shaken out with ether; after distilling off the ether a faintly yellow-colored oil remained behind, hardening to a white crystalline mass in a vacuum over sulphuric acid, and melting at 103° C. when crystallized out of benzene; after being purified by means of the acid barium salt the melting-point was raised to 105° C.; the substance was, therefore, pure and unaltered allylmalonic acid; it represented 9.591 grams or 95.9 per cent. of the acid originally used.

In the second test 7.3305 grams of allylmalonic acid were boiled in the same manner for twenty hours with a twenty per cent. solution of caustic soda representing ten times the necessary amount of alkali for neutralization; allowing to cool, acidifying, shaking out with ether, recrystallizing out of benzene, and purifying by means of the acid barium salt, 7.1345 grams of pure allylmalonic acid melting at 105° C. was recovered, corresponding to 97.3 per cent. of the amount used.

The loss of four and one-tenth per cent. in the first and two and seven-tenths per cent. in the second is explained by the fact

that it is impossible to recover the last portions of the acid from its solutions by means of ether.

The identity of the acid obtained, with allylmalonic acid, was not only proven by the melting-point, but also by other physical properties, as also by its deportment on distillation.

*Preparation of Allylacetic Acid.*—Zeidler[1] first obtained allylacetic acid from allylacetic acid ester and dry sodium ethylate, and stated its boiling-point to be 182° C. Conrad,[2] who got it by distilling allylmalonic acid, found the boiling-point to be 184° C.

According to Messerschmidt,[3] who used a modification of Zeidler's method, it boiled at 187° to 189° C.

Finally Marburg[4] studied the acid obtained by means of the Conrad as well as the Zeidler-Messerschmidt methods in both their physical and chemical properties and definitely settled the boiling-point at 186° to 187° C.

The allylacetic acid used in these researches was made after Conrad's process; it boiled constantly at 186° to 187° C. The production was about sixty-two per cent. of the theory.

*Boiling of Allylacetic Acid with Caustic Soda Solution.*—Ten grams of pure allylacetic acid boiling at 186° to 187° C. was boiled (in a copper flask connected with a return condenser) with ten times the amount of caustic soda necessary to neutralize it, in ten per cent. solution for twenty hours.

The cold contents of the flask were then strongly acidified with sulphuric acid and shaken out with ether, after distilling off the latter the residual acid was distilled with steam.

According to the statement given in the beginning of this paper one must consider the presence of $\beta\ \gamma$, and $\alpha\ \beta$, as well as of an oxy acid, and the use of steam was considered the better means of effecting their separation.

The distillation was continued until the distillate reacted neutral, the residual liquid in the distillation flask being then shaken out with ether; by this latter process nothing could be extracted; no oxy acid had, therefore, been formed.

The aqueous distillate was neutralized with barium carbonate

[1] *Ann. Chem.*, 187, 4. [2] Ibid, 204, 170.
[3] Ibid, 208, 93. [4] Dissertation, Strassburg, *1887*.

in the cold, boiled, filtered, and evaporated to dryness; in this manner 15.85 grams of barium salt dried at 100° was obtained. The finely powdered salt was repeatedly extracted with hot absolute alcohol, thereby one and a half grams dissolved, remaining as an amorphous yellow-colored transparent mass, upon distilling off the alcohol. Redissolved in alcohol and allowed to evaporate in a desiccator it was again deposited amorphous. This experiment gave, therefore, 90.5 per cent. of barium salt insoluble in alcohol.

In order to obtain a larger amount of the soluble salt a second trial was begun under the same conditions as the first with ten grams of allylacetic acid; it gave 16.52 grams of dry barium salt of which one gram was soluble in hot alcohol leaving ninety-four per cent. undissolved. The two portions of insoluble barium salt were mixed, and a careful fractional crystallization begun. This process allowed of the eventual separation of the $\beta\ \gamma$ and $\alpha\ \beta$ acids from the barium allylacetate. To this end the salt was dissolved in the least possible amount of hot water, filtered, evaporated to a pellicle, and allowed to crystallize.

The first crystals obtained were flat and lanceolate prisms, later flat curved needles and leaves were shot out; an easily soluble salt could, however, not be detected.

The difference in appearance of the crystals would not necessarily point to the presence of different salts, since, on the one hand, pure barium allylacetate separates out in entirely different forms according as it crystallizes out more rapidly or slowly, and on the other hand, the last fractions could, when dissolved in water, adding alcohol until precipitation began, warming and then allowing to cool slowly, be obtained in small needle-shaped crystals of exactly the same appearance.

To examine the acid the several crystallizations together with their mother-liquors were mixed, the alcohol distilled off, and the organic acid set free and removed by successive treatments with hydrochloric acid and ether, the ethereal solution shaken with calcium chloride, filtered, and distilled from a small flask, the principal portion passed over from 186° to 187° C., a higher boiling fraction not occurring.

Because the barium salt had lost considerable in weight in

the successive evaporations (due to a slight decomposition) a third trial of boiling the allylacetic acid with caustic soda was made, in order to exclude any doubt of its conversion into $\beta\gamma$ or $\alpha\beta$ acid.

13.65 grams of allylacetic acid boiling at 186° to 187° C. and which had been recovered from former trials, were boiled with twenty per cent. sodium hydroxide for twenty-two hours, in the same manner as the others had been; also here the ether extract was entirely volatile, leaving no trace of an oxy acid.

The aqueous acid distillate was made slightly alkaline with sodium carbonate, evaporated to dryness, the sodium salt so obtained decomposed with sulphuric acid and extracted with ether. The etheral extract was dried and gave 11.96 grams of an acid boiling at 186° to 187° C.; portions of a higher boiling-point were not present.

To more closely characterize the distillate 2.96 grams of the fraction boiling at 186° to 187° C., were subjected to the well-known "Lactone Reaction." For this purpose the acid was mixed with five times its weight of dilute sulphuric acid (one volume concentrated sulphuric acid and one volume water) in a small flask and heated just to boiling for fifteen minutes with constant agitation. The organic acid, which at first swam on the surface of the mixture, soon dissolved with a yellow coloration of the liquid; the contents of the flask was diluted with an equal volume of water and boiled for fifteen minutes, then cooled and extracted with ether.

The ethereal extract was dissolved in a little water, made slightly alkaline with sodium carbonate and at once shaken out with ether, a yellow-colored neutral liquid resulting, which, after drying, boiled constantly at 206° C., proving it to be pure valero-lactone produced from the unaltered allylacetic acid.

The alkaline solution freed from lactone was, after removing the ether, acidified with sulphuric acid and distilled with steam; the distillate after neutralizing with calcium carbonate, filtering, and evaporating to dryness gave 0.1352 gram of a gray residue equivalent to 4.57 per cent. of the acid used.

From these three trials one can certainly conclude that by boiling allylacetic acid with caustic soda, neither propylidene-

acetic acid, nor ethylidenepropionic acid, nor an oxy acid is formed in any quantity, which can be detected.

If a change does at all occur it is almost imperceptible. The small quantities of a barium salt soluble in alcohol were not sufficient to settle the question, whether it was the salt of the $\alpha\ \beta$ acid.

## PART II.

The ethylidenepropionic acid, $CH_3—CH=CH—CH_2—COOH$ was prepared according to Fraenkel[1] by the distillation of methylparaconic acid.

*Preparation of Methylparaconic Acid.*--Methylparaconic acid was first made by Gantter[2] from acetosuccinic acid ester, by reducing with sodium amalgam and described under the name of ethylidene hydroxysuccinic acid. Fraenkel,[3] however, was the first one who obtained it pure; he prepared it by the condensation of acetaldehyde with sodium succinate; he also described it more closely.

The acid used in the present research was prepared according to Gantter's method, and since the preparation is somewhat difficult it may not be amiss to give it more than a casual description here.

1. Monochloracetic acid ester, was obtained after the Conrad[4] process; it gave a yield of eighty-five per cent. of the theoretical amount.

2. The acetosuccinic acid ester, was prepared according to Conrad's[5] process, which by fractioning under reduced pressure gave upwards of sixty per cent. of the theory.

In the acetosuccinic acid ester synthesis, it is of advantage to add the acetic acid ester, as well as the monochloracetic acid ester as rapidly as possible through a stoppered funnel into a flask containing the sodium ethylate and connected with a return condenser; by so doing the violent bumping of the contents of the flask is prevented; this can only otherwise be accomplished by filtering off the sodium chloride, which separates out in the reaction.

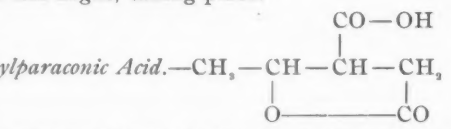
After the two esters have been brought together, the contents

[1] *Ann. Chem.*, 255, 24. [2] Dissertation, Wuerzburg, *1878*. [3] Ibid, 255, 18.
[4] Ibid, 188, 218. [5] *Ann. Chem.*, 188, 218.

of the flask are kept boiling on the water-bath for two hours, allowed to cool, mixed with ice-water, and extracted with ether; a reddish-brown crude ester is obtained, which, after being shaken with small portions of water, is subjected to fractional distillation. Drying by the use of calcium chloride is not to be recommended, since the salt dissolves, and when distilled, causes a decomposition of the ester, as Gottstein[1] and Young[2] have also observed in similar esters.

To free the crude ester of ether, alcohol, water, unaltered acetic acid ester, and monochloracetic acid ester, it was heated to 200° C. That portion, which did not distill off at this temperature, was then fractioned in a rarefied atmosphere under fifty mm. pressure and this repeated three times, gave an ester boiling at 180° to 183° C.

This was accepted as pure acetosuccinic acid ester; it presented a colorless pleasant smelling liquid almost as thick as glycerol. By fractioning under the ordinary pressure it was never found possible to obtain an ester as colorless, nor boiling as constantly, and notwithstanding the statements of Conrad[3] it is the author's opinion that it can not be distilled under ordinary pressure even when perfectly pure, without a decomposition more or less slight, taking place.

*Methylparaconic Acid.*— 

Pure acetosuccinic acid ester, in portions of twenty-five grams each, was mixed with a like quantity of absolute alcohol, and water added to a turbidity, then four per cent. sodium amalgam was added, the vessel being frequently agitated. At the beginning the sodium amalgam melted in a short time without any perceptible evolution of gas; when the reaction diminished in consequence of the concentration of the liquid more water was added until turbidity again appeared and the reaction renewed.

The mercury resulting from the decomposition of the amalgam was taken out from time to time with a pipette, washed with water, and the wash-water added to the original reducing fluid.

[1] Ibid, 216, 31-36. [2] Ibid, 216, 43. [3] *Ann. Chem.*, 188, 218.

The latter was, during the process of reduction, neutralized with dilute sulphuric acid to prevent the accumulation of a large excess of alkali. The entire process was continued until three times the theoretical amount of sodium amalgam had been added.

It is necessary in the reduction to observe that the solution does not become too warm (for this reason it may be well to set the vessel containing it, into ice-water at the beginning), also that it does not become too alkaline, otherwise a splitting of the acetosuccinic acid ester can easily occur, which, according to Wislicenus,[1] can follow in two directions.

When the sodium amalgam had ceased to act the liquid was, after removing and washing the mercury, exactly neutralized with dilute sulphuric acid, filtered, evaporated to a small volume, and allowed to crystallize, the mother-liquor drained off from the crystals of sodium sulphate, acidulated with sulphuric acid, and extracted with ether; the ethereal residue at first a yellow oil, soon becomes a solid mass when placed in a vacuum over sulphuric acid. This solid mass relieved of the oily matters by suction with a filter pump and pressure between bibulous paper gave, when broken into small pieces and kept over sulphuric acid in a vacuum, a perfectly dry white powder; this was the desired methylparaconic acid.

It was crystallized out of benzene in the following manner: A flask containing the powdered acid and some benzene, and fitted with a perforated cork, through which passed a long glass tube, was heated by plunging it into boiling water, it being constantly agitated, so as to bring the now melted underlying acid into intimate contact with the supernatant solvent; allowed to settle, and the clear solution decanted (from the liquid and still undissolved acid) into flasks, which were at once stoppered and set aside to crystallize. To the still undissolved acid in the first flask more benzene was added and the same process continued until no more was dissolved.

If before being dissolved in the benzene the acid was perfectly dry and therefore free from all oily matters then it dissolves completely and crystallizes out in hard dry crystals; if, however,

[1] Ibid, 190, 275.

the oil has not been entirely removed, then the acid separates out as a sticky mass; should this be the case then it must be freed from the solvent, the oil thoroughly removed by pressing between bibulous paper, drying, and again crystallizing out of benzene.

The production of pure acid was twenty per cent. of the theoretical.

*Preparation of Ethylidenepropionic Acid.*—The ethylidenepropionic acid was made according to Fraenkel.[1] Pure methylparaconic acid, in portions of fifteen grams each, was carefully heated in a small distillation flask; at first the acid melted to a colorless fluid, but took on a yellowish-red coloration as the operation advanced. When the temperature of the molten acid had reached 200° C. a slight evolution of carbon dioxide had begun and as the immersed thermometer indicated 240° to 260° C. the evolution of gas was a very regular one.

The thermometer bulb was now drawn up to the opening of the exit tube and the distillation continued to the end, the vapors passing over at 210° to 220° C. A slight carbonaceous residue representing nine-tenths per cent. of the acid used, alone remained behind.

The distillate, a yellowish oil of a strong empyreumatic odor contains:

1. Valerolactone.
2. Ethylidenepropionic acid.
3. Methylcitraconic acid.
4. Methylitaconic acid, and
5. Unaltered Methylparaconic acid.

1. *Valerolactone.*—$CH_3—CH—CH_2—CH_2$
$\quad\quad\quad

*2. The Acids.*—The alkaline solution, from which the lactone had been extracted, was acidulated with sulphuric acid and completely extracted with ether; the acid mixture so obtained was distilled with steam until the distillate ceased to be acid. The slightly turbid distillate was made faintly alkaline with barium hydroxide, treated with carbonic acid gas, boiled, and filtered; in this manner a solution of barium ethylidenepropionate and methylcitraconate was obtained, which can be separated by fractional crystallization.

The acid residue left in the distillation flask after distilling with steam, was evaporated to a small bulk, when it solidified to a yellow crystalline mass on being placed over sulphuric acid in a vacuum.

By treating this mass with cold chloroform the unaltered methylparaconic acid was easily extracted, while the methylitaconic acid, which was present only in small quantities, remained undissolved as a powder; the latter, like the methylcitraconic acid, was not used further.

To separate the barium methylcitraconate from the barium ethylidenepropionate, the solution containing both was simply evaporated when the barium methylcitraconate difficultly soluble in the heat separated out; it was then filtered again, evaporated, and so continued until no more salt difficultly soluble in the heat, separated out. The mother-liquors deposited upon further evaporation, when cold, the barium ethylidenepropionate in the form of flat lanceolate prisms grouped together into stars. To remove every trace of barium methylcitraconate, the barium ethylidenepropionate was recrystallized three times. It was then exactly decomposed with a weak solution of sodium sulphate, and thereby, after filtering and evaporating, sodium ethylidenepropionate obtained, in which form it was later mostly used.

200 grams of methylparaconic acid gave about forty-five grams, or twenty-two and one-half per cent. of ethylidenepropionic acid.

*Preparation of Propylideneacetic Acid.*—By the action of propionaldehyde on malonic acid Komnenos[1] obtained a monobasic unsaturated acid with five atoms of carbon, which he called pro-

[1] *Ann. Chem.*, **218**, 166.

pylideneacetic acid. In the same manner Zincke and Kuester,[1] as well as Ott[2] and Viefhaus,[3] prepared their propylideneacetic acid.

Zincke and Kuester[4] also obtained, in an entirely different manner, an acid which they recognized to be identical with Komnenos's propylideneacetic acid.

Starting with hexachlordiketo R hexane obtained from catechol, orthoamidophenol and chlorine they prepared successively tetrachlorcatechol or tetrachloramidophenol, and then pentachlorbutane carbon dioxide, and by treating the latter with sodium amalgam, procured their acid.

Fittig and Fraenkel,[5] however, suspected that the above acid of Zincke and Kuester was identical with ethylidenepropionic acid, obtained from methylparaconic acid; this supposition was, through the later researches of Zincke and Kuester,[6] made very probable, inasmuch as these investigators obtained small quantities of lactone by treating the bromhydric acid addition product of their acid with water, from which it would appear that the acid must be ethylidenepropionic acid or at least contain it as an impurity, since pure propylideneacetic acid can produce no lactone.

Such acids as have been prepared and described under the name of propylideneacetic acid are no homogeneous bodies. It was not until the writer, in July, 1892, procured the acid in its crystalline form by boiling ethylidenepropionic acid with caustic soda; and Mackenzie,[7] in February, 1893, secured it after the method of Komnenos that pure propylideneacetic acid had been made and characterized.

*Boiling of Ethylidenepropionic Acid with Sodium Hydroxide.*— Sodium ethylidenepropionate, in portions of ten grams each, was boiled with thirty-three grams of sodium hydroxide dissolved in 295 grams of water for fifteen hours in a copper flask connected with a return condenser. The cold alkaline solution was now acidulated with ether, the ethereal extract distilled with steam until the distillate came over perfectly neutral; the milky acid

1 *Ber. d. chem. Ges.*, **22**, 494. Ibid, **23**, 818. Ibid, **24**, 909.
2 Ibid, **24**, 2,600. 3 Ibid, **26**, 915. 4 Ibid, **21**, 2,719.
5 Ibid, **255**, 33. 6 *Ber. d. chem. Ges.*, **24**, 909.
7 Dissertation, Strassburg, 1894.

distillate was neutralized with barium carbonate in the cold, filtered, and evaporated to dryness.

From the liquid remaining in the distillation flask the $\beta$ oxyvalerianic acid was obtained (see $\beta$ oxyvalerianic acid).

To separate the ethylidenepropionic acid and expected propylideneacetic acids, the dry barium salt was repeatedly extracted with hot alcohol and filtered hot each time; the barium salt remaining undissolved was perfectly white and proved to be unaltered barium ethylidenepropionate; it was through double decomposition with sodium sulphate changed to the sodium salt, in which form it was again boiled with caustic soda. In the alcohol another barium salt had been dissolved; on distilling off the solvent a light yellow-colored, amorphous varnish-like mass was left behind; this was supposed to be the barium salt of the newly formed $\alpha\ \beta$ acid.

To remove every trace of $\beta\ \gamma$ acid from it, the barium salt was decomposed with sodium sulphate forming the sodium salt, and this mixed with a quantity of dilute sulphuric acid (one volume concentrated sulphuric acid and one volume of water), corresponding to five tiines the amount of organic matter present, plus a sufficiency to neutralize the sodium of the sodium salt and heated in a flask almost to boiling, with constant agitation for fifteen minutes, then mixed with a like bulk of water and boiled for thirty minutes. Allowed to cool, the acid solution is extracted with ether, the ethereal extract again rapidly boiled with some water, and a few drops of dilute sulphuric acid to again change into lactone any oxy acid, which may have been formed, rapidly cooled off, sodium carbonate added to an alkaline reaction, and the lactone at once shaken out with ether. The alkaline solution free from lactone was again acidified, extracted with ether, and the ethereal residue distilled with steam, the acid distillate neutralized with sodium carbonate anew, and the sodium salt obtained, again treated with sulphuric acid as above. The entire operation was repeated until no more lactone was formed; this was accomplished after repeating it two or three times, when every trace of $\beta\ \gamma$ acid had surely been removed.

Propylideneacetic acid: $CH_3-CH_2-CH=CH-COOH$.

After no more lactone could be detected in shaking the alka-

line liquid after boiling with sulphuric acid, the solution was acidified and distilled with steam, and from the acid distillate the sodium or calcium salt of the $\alpha\,\beta$ acid produced. On decomposing the sodium salt with sulphuric acid, or the calcium salt with hydrochloric acid in a narrow tube, the pure $\alpha\,\beta$ acid was obtained as an almost colorless oily layer; it was drawn off, the last portions extracted with ether, and the ethereal solutions dried by means of dried sodium sulphate or calcium chloride, filtered, and the ether evaporated, leaving a colorless oil, which congeals in a freezing mixture at once and remaining solid indefinitely in ice-water, since it melts at $7\frac{1}{4}°$ to $8\frac{1}{4}°$ C.

In cold winter weather it is extremely easy to obtain the acid perfectly pure and of the correct melting point.

The acid from the ethereal extract is poured into a watch-glass and placed in a desiccator at a low temperature; it then solidifies in flat rhombohedral tables or leaves, which can, with the aid of a cold platinum wire, be brought upon a piece of filter paper, to there give up the last traces of moisture, remaining behind as flat, glistening crystals. The acid is therefore the $\alpha\,\beta$ acid, corresponding to the ethylidenepropionic acid; its melting-point, compared with a specimen of the acid subsequently prepared, after the method of Komnenos,[1] which was purified and crystallized in a like manner, gave the following results.

A specimen of each was placed on the bulb of the same thermometer and plunged into a freezing mixture for a minute and then into cold water, the temperature of which was gradually raised.

At $6\frac{1}{2}°$ C. they both remained solid.

At 7° C. likewise so.

At $7\frac{1}{4}°$ C. both samples began to melt slightly.

At $7\frac{1}{2}°$ C. both were about half melted.

At 8° C. only a small quantity of each still remained solid.

At $8\frac{1}{4}°$ C. both were completely melted.

The melting-point determinations were made by placing the acid in thin-walled melting-point tubes two mm. in diameter, and closed at both ends; this allowed of a repetition of the esti-

[1] *Ann. Chem.*, **218**, 166.

mations without any danger of loss by evaporation or inaccuracy from the absorption of water.

During some recent work on propylideneacetic acid by the Komnenos' process, Mackenzie[1] found the melting-point to be $9\frac{1}{2}°$–$10\frac{1}{2}°$ C.

It is much more difficult to obtain the solid acid of a constant melting-point in summer; to this end the following method was used: The acid freed, as much as possible, from ether and water, contained in a small flask held horizontally, was moved backwards and forwards through a water-bath of 65° C., in order to remove the last traces of ether. The flask was then closed with a stopper and calcium chloride tube, and plunged into a freezing mixture of ice and salt, in such a manner that the acid congeals on one side of the flask; the flask was now placed upright in a vessel of ice-water for an hour; the mother-liquor draining out was poured off; finally the crystalline cake was itself slightly warmed, so that the last low melting portions of the acid percolated out what remained congealed in a freezing mixture completely and did not remelt in ice-water.

Pure propylideneacetic acid becomes solid at 0° C.; if the melted acid be placed in ice-water, it solidifies in half an hour. If a crystal of the acid be dropped in, it congeals at once. The smallest quantities of water or ether have a decided effect on its melting-point.

At the ordinary temperature pure propylideneacetic acid is a mobile colorless liquid with a faint, pleasant odor of acetic acid. It is so volatile, that even at 45° C. it passes over with the ether vapors, and in summer a considerable loss is not to be prevented when working with this substance.

About sixty per cent. of the ethylidenepropionic acid is converted into propylideneacetic acid by boiling with caustic soda. For analysis the acid melting at $7\frac{1}{4}°$ to $8\frac{1}{4}°$ C. was used.

1. 0.2716 gram acid gave 0.1915 gram $H_2O$, and 0.595 gram $CO_2$.

2. 0.2965 gram acid gave 0.2125 gram $H_2O$, and 0.6508 gram $CO_2$.

[1] Dissertation, Strassburg, 1894.

| | Calculated for $C_5H_8O_2$. | Found. 1. | 2 |
|---|---|---|---|
| C ..... | 60.00 | 59.75 per cent. | 59.86 per cent. |
| H ..... | 8.00 | 7.84 " | 7.96 " |

*Salts of Propylideneacetic Acid.*—Barium Salt. The barium salt of propylideneacetic acid is very characteristic; it was prepared by neutralizing propylideneacetic acid with barium carbonate suspended in water; the neutral solution was boiled, filtered, and evaporated to a pellicle; after cooling, the pellicle was removed from the surface of the solution and the liquid placed in an ice-chest (for when allowed to evaporate at the ordinary temperature a sticky mass only separates out) to undergo a very slow evaporation. After some weeks the salt is deposited in needles grouped to rosettes; these were washed and subjected to analysis.

The salt contains considerable water of crystallization, but effloresces easily, becoming anhydrous in a desiccator over sulphuric acid.

1. The salt pressed between filter paper and allowed to remain in an ice-chest on a piece of filter paper over night, was on the following morning weighed into an open crucible, and allowed to remain in a desiccator to constant weight.

0.2102 gram lost 0.0170 gram $H_2O$ or 8.10 per cent.

2. The pressed salt was, after remaining for fifteen minutes on a piece of filter paper in the ice-chest, weighed into an open crucible and allowed to remain to constant weight in a desiccator.

0.6470 gram lost 0.1028 gram $H_2O$ or 15.88 per cent.

3. The pressed salt was placed for twenty-five minutes in the air at 14° C. and then treated as above.

0.2493 gram lost 0.0203 gram $H_2O$ or 8.14 per cent.

4. 0.1932 gram of the salt dried in a desiccator gave 0.1335 gram $BaSO_4$, 0.0785 gram Ba.

| Calculated for $(C_5H_7O_2)_2$ Ba. | Found. |
|---|---|
| 40.89 per cent. Ba. | 40.63 per cent. Ba. |

It follows from these determinations that because of the disposition of this salt to effloresce, it is impossible to make an exact estimation of the water; the difference in amount seems to depend on the temperature at which the crystallization takes place.

It was found impossible to examine the crystals optically; one can only see that they are tables with end faces, but to which system they belong can not be said.

To observe the deportment of the crystallized salt at a higher temperature, a portion which had crystallized out in the ice-chest was placed together with its mother-liquor in a stoppered vessel and allowed to remain several days at a temperature of 20° C.; a part of the crystals were thereby dissolved; the other portion, however, remained crystalline and did not become sticky.

Calcium Salt. The calcium salt was made by neutralizing an aqueous solution of the acid with calcium carbonate in the cold; the solution boiled, filtered, and evaporated to a pellicle; on cooling, the salt crystallized out in moderately long, flat, glistening prisms; they were collected on a platinum cone, washed, dried, and laid on filter paper for twelve hours at 6° C. The salt gives off all its water of crystallization in a desiccator.

0.4155 gram gave 0.0985 gram $H_2O$.

| Calculated for $(C_5H_7O_2)_2Ca+4H_2O$. | Found. |
|---|---|
| 23.22 per cent. $H_2O$. | 23.71 per cent. |

0.2263 gram of salt dried at 100° C. gave 0.1298 gram $CaSO_4$.

| Calculated for $(C_5H_7O_2)_2Ca$. | Found. |
|---|---|
| 16.81 per cent. Ca. | 16.87 per cent. Ca. |

The calcium salt crystallizes much easier than the barium salt, since it can be obtained at a temperature of 16° C. in nice prisms, while the barium salt always becomes sticky at this temperature. Calcium propylideneacetate like the barium salt is easily soluble in water and alcohol.

*Propylideneacetic acid dibromide.*

$\alpha\ \beta$ dibromvalerianic acid.

$\alpha\ \beta$ pentinic acid dibromide.

$CH_3-CH_2-CHBr-CHBr-COOH$.

To further characterize the acid, the bromine and bromhydric acid addition products were made.

To prepare the dibromide, the vessels and reagents used were carefully dried.

The acid was dissolved in a little carbon disulphide and then with exclusion of air the calculated amount of bromine in a ten per cent. carbon disulphide solution was added through a drop-

per funnel-tube. A violent reaction was not noticed even at the commencement, the decolorization being slow and incomplete. The experiment was conducted in diffused daylight.

After a small excess of bromine had been added, the whole was cooled off and allowed to remain quiet for twenty-four hours; the most of the carbon disulphide was then removed by aspirating a current of dry air through the bottle; the remaining solution was placed on a large watch-glass in a desiccator, and the disulphide entirely removed by frequent stirring with a glass rod. The desiccator placed in a refrigerator soon caused the dibromide to crystallize out in large leaves.

After the disulphide had been completely removed by alternate stirring, and evacuation of the desiccator, the solid dibromide was dissolved in the least possible quantity of petroleum ether, and the solution allowed to stand in a corked test-tube for several hours. Here the dibromide was deposited in rosettes of flat prisms on the sides of the tube. The mother-liquor was rapidly decanted and the crystals washed two or three times with cold (0° C.) petroleum ether, and again crystallized out of the latter, when the preparation was considered pure.

The dibromide seems not adapted for crystallographic study; the crystallization is probably monosymmetric; it melts without coloration at 56° C.; it is very soluble in carbon disulphide and benzene; in petroleum ether it is easily soluble.

0.2040 gram of the dibromide dried in a vacuum gave 0.2957 gram of AgBr = 0.1258 gram Br.

| Calculated for $C_5H_8Br_2O_2$. | Found. |
|---|---|
| 61.54 per cent. Br. | 61.68 per cent. Br. |

$\beta$ Bromvalerianic acid. $CH_3-CH_2-CHBr-CH_2-COOH$.

The hydrobromic acid addition product of propylideneacetic acid was prepared as follows: To one volume of the pure acid contained in a small cylinder having a well-ground stopper, one and a half volumes of hydrobromic acid saturated at 0° C. were added; on shaking, a clear solution resulted; it was allowed to remain quietly for twenty-four hours at the ordinary temperature; the monobromide had now risen to the surface of the hydrobromic acid as a light brown-colored layer. The cylinder was now vigorously shaken from time to time, to bring any

unaltered propylideneacetic acid which might be dissolved in the monobromide, into intimate contact with the hydrobromic acid. After this occasional shaking had been continued four or five days, the contents of the cylinder formed two distinct layers; the reaction was ended and all the propylideneacetic acid had been quantitatively changed into β bromvalerianic acid. The cylinder, still stoppered, was now placed in ice-water to cause the new acid to solidify, this, however, did not occur. It was then placed in a freezing mixture of ice and salt, and on agitating slightly, the monobromide at once congealed to a mass of fine needles lying on the surface of the hydrobromic acid. The cylinder stood for fifteen hours at a temperature of 15° C.; then the crystalline cake was broken through with a glass rod, distributed through the hydrobromic acid, and brought into a platinum cone where it was allowed to dry, being washed with small successive portions of ice-water, in order to remove the greater part of the mineral acid. The contents of the cone were now brought upon a watch-glass and placed in a vacuum over sulphuric acid and potassium hydroxide; a dry sandy-white substance resulted, which was powdered and recrystallized out of petroleum ether. So produced, the β bromvalerianic acid is, after drying, perfectly pure, as the analysis proves.

0.233 gram of the substance dried in a vacuum gave 0.2410 gram AgBr.

| Calculated for $C_5H_9BrO_2$. | Found. |
|---|---|
| 44.20 per cent. Br. | 44.20 per cent. Br. |

β bromvalerianic acid melts at 59° to 60° C., the melting-point not altering in the least by repeated determinations on the same sample.

It dissolves readily in ether, chloroform, carbon disulphide, less easily in benzene and petroleum ether, and is almost insoluble in water of 0° C.

If the cold, saturated solution of the monobromide in petroleum ether be allowed to evaporate spontaneously it crystallizes out in beautiful, colorless, eight-sided prisms.

The crystals set up after Naumann's system give the following crystallographic measurements:

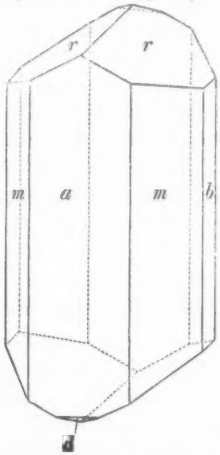
## β Bromvalerianic Acid.

Crystal system : Monosymmetric.

$$\dot{a} : \bar{b} : \dot{c} = 1.4688 : 1 : 0.4900$$

$$\beta = 79^\circ 58' 45''$$

Observed forms: $m = \{110\}\ \infty P$, $a = \{100\}\ \infty \bar{P}\infty$, $b = \{010\}\ \infty \dot{P}\infty$, $r = \{011\}\ \bar{P}\infty$, $d = \{\bar{1}01\} + \bar{P}\infty$, $e = \{101\} - P\infty$.




The crystals are mostly two to five mm. long by one to two mm. wide, and possess a valerianic acid-like odor.

Some crystals are minus $[\bar{1}01] + \bar{P}\infty$, as also $[100]\ \infty \bar{P}\infty$, while $[10\bar{1}] - \bar{P}\infty$ was only observed once.

The faces were almost always smooth and polished, giving excellent reflexes.

The following angles were measured and calculated:

| | Measured. | Calculated. |
|---|---|---|
| r : r = (011) : (011) = | *51° 31′ | ..... |
| a : m = (100) : (110) = | *55° 20′ 30″ | ..... |
| r : m = (011) : ($\bar{1}$00) = | *99° 1′ | ..... |
| m : m = (110) : (1$\bar{1}$0) = | 110° 43′ | 110° 41′ |
| m : b = (110) : (010) = | 34° 47′ | 34° 39′ 30″ |
| r : b = (011) : (010) = | 64° 6′ | 64° 14′ 30″ |
| a : b = (100) : (010) = | 89° 58′ | 90° |
| a : d = (100) : ($\bar{1}$01) = | 99° 2′ | 99° 12′ |

| | Measured. | Calculated. |
|---|---|---|
| $r : m = (011) : (1\bar{1}0) =$ | 74° 2′ | 74° 26′ |
| $a : e = (100) : (101) =$ | 61° 59′ | 62° 44′ |
| $r : d = (101) : (\bar{1}01) =$ | 36° 33′ | 36° 29′ |
| $r : m = (011) : (110) =$ | 63° 33′ | 63° 28′ |
| $r : d = (011) : (\bar{1}01) =$ | 31° 8′ | 31° 45′ |
| $d : m = (\bar{1}01) : (\bar{1}00) =$ | 80° 11′ | 80° 48′ |

A cleavage could not be found. The plane of the optical axes stands at right angles to the klinopinacoid and is only slightly inclined towards the orthopinacoid.

Obtuse bisectrix = b axis.

*β* Oxyvalerianic acid, $CH_3—CH_2—CH(OH)—CH_2—COOH$.

The acid mixture from the treatment of ethylidenepropionic with caustic soda was not completely volatile with steam.

The residue left in the distillation flask, after the ethylidenepropionic and propylideneacetic acid had been driven over, had a strong acid reaction and gave up a yellow oil when shaken with ether. It was purified by dissolving in ether and precipitating with petroleum ether as a thick colorless liquid. This syrup could not be solidified either by allowing it to remain in a desiccator or at a temperature of 18° C. for several hours, aided by frequent stirring with a platinum wire. A portion of the acid, which had been prepared from the perfectly pure barium salt, was dried in a desiccator to constant weight; it then presented an absolutely colorless liquid, which, when put into a narrow test-tube and placed in a freezing mixture, would not become solid with frequent stirring by means of a platinum wire. At best it remained a colorless molasses-like liquid, although the barium salt from which it was obtained as well as the acid itself, as far as purity is concerned, left nothing to be desired as the analyses show.

0.2745 gram obtained from the pure barium salt contained in a platinum boat and dried in a desiccator gave 0.2073 gram $H_2O$ + 0.5105 gram $CO_2$.

| | Calculated for $C_5H_{10}O_3$. | Found. |
|---|---|---|
| C | 50.85 per cent. | 50.72 per cent. |
| H | 8.47 " | 8.39 " |

*β* oxyvalerianic acid is easily soluble in cold water, ether, benzene, and in chloroform; in carbon disulphide and petroleum ether it is insoluble.

From forty-five grams of ethylidenepropionic acid, which was boiled with caustic soda, 16.5 grams or thirty-six per cent. of $\beta$ oxyvalerianic acid was produced.

*Salts of $\beta$ Oxyvalerianic Acid.*—Calcium Salt. The still yellow-colored acid was diluted with water and heated on the water-bath until the mixture reacted neutral; it was then filtered and the yellow-colored filtrate decolorized with animal charcoal; the filtered solution was now evaporated until a pellicle formed on the surface and was then allowed to cool; the pellicle was dissolved and after remaining at the ordinary temperature for some time there was deposited on the bottom of the vessel a collection of white opaque warts of porcelain-like appearance, which, when powdered and dried in the air, was analyzed.

1. 0.43 gram of air-dried salt lost 0.0263 gram $H_2O$ at 175° C.

| Calculated for $(C_5H_9O_2)_2Ca+H_2O$. | Found. |
|---|---|
| 6.16 per cent. $H_2O$. | 6.12 per cent. |

2. 0.1889 gram anhydrous salt gave 0.0915 gram $CaSO_4$.

| Calculated for $(C_5H_9O_2)_2Ca$. | Found. |
|---|---|
| 14.59 per cent. Ca. | 14.30 per cent. |

The salt retains its water of crystallization very tenaciously and gives it up when heated for some time at 175° C. At 180° C. it begins to melt and acquire a yellow tint, whereby it loses considerable in weight and at 200° C. a yellow transparent molten mass filled with bubbles results, with an increase in the amount of decomposition, which began at 180° C. The salt is quite soluble in water and insoluble in alcohol. Still the aqueous solution, to which three volumes of absolute alcohol has been added, remains perfectly clear at first, only becoming cloudy after the lapse of some hours, and after a longer period the salt is deposited as a sandy indistinctly crystalline mass.

Treated with alcohol on a slide and examined under the microscope the following was observed:

The precipitate consists of small, mostly irregularly formed, double refracting leaves, stretched at times in one direction, and which present an oblique obliteration of light, parallel to this principal direction of development. Because of this oblique obliteration the crystals probably belong to the monoclinic system.

Barium Salt.—The barium salt was prepared in exactly the same manner as the preceding, by warm neutralization of

barium carbonate; the solution evaporated to a pellicle, was allowed to cool, the pellicle not dissolving; after about an hour it became cloudy, and deposited small, fine needles, which gradually accumulated on the bottom of the beaker as a sandy crystalline mass.

This crystalline mass treated with alcohol and examined under the microscope, showed a colorless, strongly double refracting homogeneous number of crystals, grouped to a half ball; they were tables of rhombic or right angular form, with an oblique obliteration and were, therefore, probably monoclinic.

0.1983 gram of the air-dried salt lost 0.0093 gram $H_2O$ at 105° C. and gave 0.1193 gram $BaSO_4$.

| | Calculated for $(C_5H_9O_3)_2$ Ba+$H_2O$. | Found. |
|---|---|---|
| $H_2O$ | 4.63 per cent. | 4.67 per cent. |
| Ba | 35.22 " | 35.36 " |

At 105° C. the salt melts without decomposition to a colorless transparent mass; even, on the water-bath, when covered with a little water a thick syrup results. It is insoluble in alcohol.

Silver Salt.—The silver salt was obtained by the double decomposition of a warm concentrated solution of the calcium salt with silver nitrate, as slightly violet-colored crystals or a powder according as it separated out rapidly or slowly. When recrystallized from hot water it is nearly white and is but little affected by light.

0.1037 gram of the salt dried at 50° to 55° C. gave in the combustion 0.0497 gram Ag.; 0.1018 gram $CO_2$; and 0.0390 gram $H_2O$.

| | Calculated for $(C_5H_9O_3)$Ag. | Found. |
|---|---|---|
| Ag. | 48.00 per cent. | 47.93 per cent. |
| C | 26.67 " | 26.86 " |
| H | 4.00 " | 4.27 " |

Microscopically the crystalline powder appeared to be fine, flat, at times, corroded needles, which had an oblique obliteration in their long direction.

*Boiling β Oxyvalerianic Acid with Sodium Hydroxide.*—For this very interesting experiment 6.240 grams of calcium β oxyvalerianate (representing five grams of acid) was used; through double decomposition with sodium carbonate sodium β oxyvalerianate was formed and this boiled for thirty hours in a copper flask connected with a return condenser and containing 17.1 grams, of sodium hydroxide in 154 grams of water.

After cooling, the solution was acidified with sulphuric acid and extracted with ether. The ethereal residue rapidly boiled with water and a few drops of dilute sulphuric acid, to change any $\gamma$ oxy acid present (which could have originated from the $\beta$ oxy acid with ethylidenepropionic acid and valerolactone as intermediate steps) into lactone, was then made slightly alkaline with sodium carbonate, and shaken out with ether; nothing was taken up by the latter, consequently, the presence of $\gamma$ oxy acid must be excluded.

The alkaline solution, after the ether had been removed, was acidulated with sulphuric acid and distilled with steam until the distillate passed over the neutral. The unaltered $\beta$ oxy acid remained behind in the distillation flask, which, when shaken with ether, allowed of its removal from the contents of the same; it was converted into the calcium salt, which amounted to three and four-tenths grams or more than one-half of the acid originally employed.

The acid distillate was neutralized with barium carbonate, but since the barium salts thus obtained do not allow a good separation with alcohol, they were converted into the sodium salts through the aid of sodium sulphate, and now the $\beta\gamma$ acid converted into lactone by boiling with sulphuric acid, made alkaline with soda solution, the lactone was shaken out with ether, and characterized by boiling with barium hydroxide for thirty minutes, thus converting it into the barium salt of $\gamma$ oxyvalerianic acid. After precipitating the excess of barium with carbon dioxide in the heat, the evaporated filtrate gave 1.973 grams of an amorphous substance easily soluble in alcohol and water, from which it was deposited as a gummy mass, and proved in all its conduct to be the barium salt of $\gamma$ oxy acid. Finally by exactly precipitating with sulphuric acid in the heat, and adding potassium carbonate to the cold filtrate in a narrow tube the valerolactone was obtained as a supernatant layer.

The alkaline solution freed from lactone was acidulated with sulphuric acid and distilled with steam; from the acid distillate through neutralization with calcium carbonate 0.94 gram of calcium propylideneacetate was obtained, from which the acid itself was freed. After purifying in the manner already mentioned it melted at $7\frac{1}{4}^\circ$ to $8\frac{1}{4}^\circ$ C.

In the process of boiling with caustic soda, there was obtained from the $\beta$ oxy valerianic acid:

56.6 per cent. of unaltered oxy acid.
21.26 per cent. of ethylidenepropionic acid.
14.64 per cent. of propylideneacetic,
with a loss of 6.5 per cent.

*Distillation of the $\beta$ Oxyvalerianic Acid.*—A portion of the thick, almost colorless, acid was so distilled from a small distillation flask that it passed over slowly and in drops. As the boiling began, the thermometer with its bulb in the liquid indicated 190° C.; it was now raised until its bulb was just beneath the exit tube; it sank to 180° C., but rapidly rose to 190° C., where it remained constant for a short time, gradually rising to 195° C., and then to 200° C., where the principal portion went over, and finally to 203° C.; the last drops of the distillate were colored yellow, and a small tarry residue only remained in the flask. The distillate, which had the same empyreumatic odor as that from methylparaconic acid, was mixed with five times its volume of water and sufficient sodium carbonate to render it distinctly alkaline after a vigorous shaking; nothing could be extracted by means of the ether, consequently, the distillate contained no lactone and a conversion of $\beta$ oxyvalerianic acid into $\gamma$ oxy acid respectively $\gamma$ lactone had not taken place. The salt solution, free from ether, was now acidulated and distilled with steam, in order to separate the unsaturated acids from the oxy acid. The milky distillate was neutralized with barium carbonate and thereby the mixed barium salts of the volatile acids obtained; as, however, these can not be satisfactorily separated with alcohol, the above-described process used to effect their separation when produced by boiling the oxy acid with caustic soda was employed and the $\beta$ $\gamma$ acid separated as lactone from the $\alpha$ $\beta$ acid; the latter was characterized by means of its melting-point.

From the residue of the distillation with steam a small amount of the $\beta$ oxy acid could be extracted.

The principal product in the distillation of the $\beta$ oxyvalerianic acid was propylideneacetic acid; only a small quantity of ethylidenepropionic was found, and a like small portion of oxy acid went over unaltered.

The three isomers allylacetic, ethylidenepropionic, and pro-

After cooling, the solution was acidified with sulphuric acid and extracted with ether. The ethereal residue rapidly boiled with water and a few drops of dilute sulphuric acid, to change any $\gamma$ oxy acid present (which could have originated from the $\beta$ oxy acid with ethylidenepropionic acid and valerolactone as intermediate steps) into lactone, was then made slightly alkaline with sodium carbonate, and shaken out with ether; nothing was taken up by the latter, consequently, the presence of $\gamma$ oxy acid must be excluded.

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From the residue of the distillation with steam a small amount of the $\beta$ oxy acid could be extracted.

The principal product in the distillation of the $\beta$ oxyvalerianic acid was propylideneacetic acid; only a small quantity of ethylidenepropionic was found, and a like small portion of oxy acid went over unaltered.

The three isomers allylacetic, ethylidenepropionic, and pro-

pylideneacetic acids, can, as the accompanying table shows, be easily characterized and distinguished.

But recently Fittig and Mackenzie[1] have for the sake of simplicity, applied the terms $\gamma\ \delta$, $\beta\ \gamma$, and $\alpha\ \beta$ pentinic acids to the allylacetic, ethylidenepropionic, and propylideneacetic acids, respectively.

| | Allylacetic acid. | Ethylidenepropionic acid. | Propylideneacetic acid. |
|---|---|---|---|
| Free acid. | Fluid, boiling-point 186°-187° C., characteristic odor resembling that of valerianic acid. | Fluid, boiling-point 193°-194° C. | Solid melts at 7¼-8¼° C. |
| Calcium salt. | Crystallize out of a hot saturated aqueous solution with one molecule of water in flat pointed prisms, which are insoluble in alcohol. | | Crystallizes out of the aqueous solution in the cold, with four molecules of water of crystallization<br>Soluble in hot absolute alcohol. |
| Barium salt. | Crystallize out of a hot saturated aqueous solution with one molecule of water in flat pointed prisms. Insoluble in alcohol. | | Crystallizes in the cold out of the aqueous solution with two and four molecules of water.<br>Soluble in hot absolute alcohol. |
| Monobromide. | Both acids produce the same $\gamma$ bromvalerianic acid with hydrobromic acid. Fluid and not solid at—16° C. | | Gives with hydrobromic acid $\beta$ bromvalerianic acid. This crystallizes out of petroleum ether in monoclinic prisms with the following forms:<br>$\infty P\infty, \infty P, \infty \breve{P}\infty, \grave{P}\infty, +\bar{P}\infty, -\bar{P}\infty$,<br>melts at 59°–60° C.<br>Insoluble in water, becomes liquid in water of 45°–50° C. |
| Dibromide. | Thin four-sided monoclinic tables melting at 58°.<br>Difficultly soluble in petroleum ether. | Monoclinic prisms developed in the direction of the C axis. Readily soluble in warm petroleum ether; less so in cold. Melting-point 65°; dissolves in water with a gyratory motion. Becomes fluid under water of 50°-55° C. | Monoclinic prisms melting at 56°, becoming liquid under water of 15° C.<br>Very readily soluble in petroleum ether at the ordinary temperature. |

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[1] Dissertation, Strassburg, 1894.

# THE PHOSPHOMOLYBDIC ACID TEST AS APPLIED TO LARD ANALYSIS.

By George F. Tennille.

Received November 5, 1894.

THE phosphomolybdic acid test has been of late so strongly recommended for use in the detection of cottonseed-oil in lard that it seemed to the writer that the record of the results of a rather thorough trial of this reagent would be of interest to chemists.

The test was originally proposed by P. Welmans in the *Pharm. Zeit.*, *1891*, **36,** 798. One gram of the oil or fat was dissolved in five cc. of chloroform, two cc. of phosphomolybdic acid solution were added, and the mixture shaken. On standing, the liquid separated into two layers, the lower of which was colorless and the upper of which had become green, if any vegetable oil were present. The addition of an alkali changed the green to a blue color. Lard, tallow, goose fat, and butter fat were said not to show any green coloration, and the only animal oil which gave the test was cod-liver oil.

It was supposed that at last the reagent had been discovered which would serve to detect any addition of cottonseed or other vegetable oils to lard, no such one test having previously been satisfactory. Very shortly this reaction was recommended for such a use by a number of chemists. Among others, Engler and Rupp, Wimmer, Mansfeld, and Goske approved of its efficacy. H. Schweitzer and E. Lungwitz (*J. Soc. Chem. Ind.*, *June*, *1894*, 614) state that they have found the reagent of great use.

Wallenstein, the first to criticise the test, (*J. Soc. Chem. Ind.*, *1893*, 55) states that tallow gives a green coloration when tested with the phosphomolybdic solution. To satisfy myself in regard to this point raised by Wallenstein I have tested a large number of samples of tallow, and other qualities of beef fat—such as might be used in adulterating lard or in the manufacture of compound lard—and have in no case obtained a green color.

J. Lewkowitsch (*J. Soc. Chem. Ind.*, *June*, *1894*, 617) has made an extended series of experiments with different fats and

oils in regard to the colors given with phosphomolybdic acid. He writes in part as follows: "Of all the samples only lard had remained colorless and there seemed to be ground for the opinion that cottonseed-oil or any other seed-oil employed for adulteration might easily be detected by phosphomolybdic acid. I prepared, therefore, a number of mixtures of pure, freshly rendered lard, yielding no coloration with Welman's test and of cottonseed-oil giving a distinct blue reaction." In testing these mixtures, he found that up to those containing thirty-five per cent. of cottonseed-oil the color of the upper layer was yellow, and at thirty-five per cent., on making this test alkaline, he only obtained a faint blue coloration. He continues: "This table clearly demonstrates the necessity of using Welman's test with great caution. In practical analysis an adulteration of ten per cent. cottonseed-oil would escape detection if freshly rendered lard had been used. Indeed, pure lard mixed with fifteen per cent. cottonseed-oil gave reactions just like sample number sixty-three in the preceding table." (Sample number sixty-three was a lard slightly rancid, six years old and gave a test remaining yellow when acid, and only faintly blue when alkaline.) "Welman's reaction can therefore be admitted only as a preliminary test, the indications of which may, in some cases, give valuable hints as to the direction in which the examination of a given sample has to be carried out and may serve as a useful corroboration of results obtained by other methods."

Of course it is understood that the original color of the phosphomolybdic acid solution is a decided yellow. The green color produced by a certain sample is not of as deep a shade as the corresponding blue color when the acid has been neutralized by ammonia. Hence a light green tinge, which would be difficult to observe on account of the initial yellow color of the reagent, would be most readily seen when changed to a blue by the alkali.

Of all the samples of cottonseed-oil, which I have tested, each one gave a green color, though I find that the color varies much in depth with different oils. It seems to be a general rule that the more refined the oil the less heavy the coloration. Thus a crude oil will color intensely green, a yellow oil perhaps less so,

and a white oil still less. The age of the oil and the method of refining also in a great measure modify the color. In his tests on percentages, J. Lewkowitsch states that he used in making the mixtures a cottonseed-oil which gave a distinct blue reaction. The oil probably did not, therefore, show a deep green coloration and the test on the oil had to be made alkaline to produce a color which was decided. He must have used, I should judge, either an unusual oil or a weak solution of the reagent. For such oils as would commonly be employed for adulterations or compounding I think that ten to fifteen per cent. in a mixture would show a decided green coloration.

Samelson (*Ztschr. anal. Chem.*, *1894*, 189) comes to the conclusion that the phosphomolybdic acid test is of no value and that the iodine-absorption figure is the only reliable test for the detection of cottonseed-oil in lard. He states that six samples of American lard are undoubtedly impure because they have Hübl figures of from 64.7 to 67.2, which are higher than any figures hitherto recorded by scientific investigators for pure hog fat. On this assumption hangs the result of his investigation of Welman's test.

I have often tested lards of undoubted purity for their iodine-absorption figures and obtained results as high as from 62.7 to 66.4. On the other hand, as will be seen later, the Hübl figures for pure lard can run as low as 47.7. It must be remembered that lards are sold in large amounts in the American market which do not represent the whole fat of the hog, but simply a portion. It is a well-known fact that fats from different parts of the hog vary greatly in their iodine figures, hence, lards made from different portions of the fat would also vary. Wiley (U. S. Dept. Ag. Bul., 13, Lard and Lard Adulterations, 1889), states in order to show the great difference in the absorption power for iodine of the different fats of the hog, as follows, "For instance, a sample of intestine lard absorbed 57.34 per cent. of iodine; the leaf lard from the same animal absorbed 52.53 per cent.; the foot lard 77.28 per cent.; the head lard 85.03 per cent. In the prime steam lards mentioned the percentage of iodine absorbed was from 60.34 to 66.47 per cent., and the mean 62.86 per cent." The iodine test alone would certainly not be of much service for

the detection of vegetable oils in lard, when the iodine figure of the lard itself may vary as I have found, from 44.70 to 66.40. As may be calculated, thirty per cent. or more of cottonseed-oil could be added to a lard with an iodine figure of 44.7 without the iodine figure of the mixture reaching beyond the figures of pure lard. Hence it will be seen, I think, that the condemnation of a lard as adulterated with cottonseed-oil on the ground of a high iodine figure would be hasty and might easily be erroneous.

In the literature, then, of this test up to the present time, the preponderance of the writing is in its favor, and only two legitimate limitations are placed upon its accuracy, one, that tallow might give the same results as cottonseed-oil, and the other, that a certain comparatively small percentage of cottonseed-oil might escape detection. At first blush, one would think, therefore, that the test would be of value in preliminary examinations of samples suspected of sophistication; namely, that a negative test would show the lard contained not more than ten per cent. of cottonseed-oil, and, as the addition of less than ten per cent. would hardly pay the renderer, was, therefore, probably free from vegetable oils, and that a positive test would almost conclusively point to the presence of a vegetable adulterant.

After the careful examination of a great number of lards I have come to the conclusion that a positive test does not prove the presence of such an adulteration.

In my investigation the test has been carried out as follows:

About one gram of the melted fat is placed in a test-tube and dissolved in five cc. of pure chloroform, two cc. of a ten per cent. solution of phosphomolybdic acid are then added and the test-tube vigorously shaken. After standing, and the mixture having separated into two layers, the color of the upper liquid is observed by comparison with a test run in exactly the same manner on a sample of pure laboratory rendered lard. I do not consider a test as decisive unless a very apparent green tinge appears, relying more upon the green coloration than upon the slight blue shades produced after making doubtful greenish-colored tests alkaline with ammonia.

The lards upon which most of my tests were made were of

those grades known in New York City as No. 1 lard, Prime City lard, and Prime Western lard. A brief account of the manner in which these lards are rendered and their difference in fat composition may be of help to the better understanding of their often dissimilar chemical properties. These three grades of lard make up the bulk of the lard sold to the refiners in the vicinity of New York City.

No. 1 lard generally sells at a trifle lower figure than Prime City lard, say as a limit, half a cent per pound, though often it commands the same price. It is a harder fat than City or Western and is all steam-rendered. In color it often has a distinct green tinge and will generally carry a higher steam flavor. It is rendered by the slaughterers and is made up of gut fat with once in a while a little trimmings. No leaf lard is in it as the leaf is sold with the carcass to the butchers. After slaughtering, the fat is stripped from the still warm intestines and carefully washed and goes together with a certain proportion of trimmings to the rendering kettle, where it is subjected to steam under pressure. When the process is complete the water, etc., is drained off and the lard placed in tierces for sale. This lard is made in and about New York City, the hogs being brought from the West and slaughtered here.

Prime City lard is made by the butchers and may be either rendered in open kettles with free fire or steam-rendered in the same manner as No. 1 lard. This lard sells as a usual thing one-half cent per pound below Prime Western lard. The kettle-rendered is darker in color than the steam lard and has a characteristic taste and smell.

City lard is made of the trimmings, head fat, foot fat, backbone fat (perhaps some back fat), and any leaf which can not be sold over the counter, which fats accumulate in large amounts in the butcher shops. There is seldom any leaf lard in it as the leaf can be sold more profitably at retail for domestic rendering. The lard is usually a trifle softer than Western lard and not as good in color or flavor though better in these respects often than the No. 1 lard.

Prime Western lard is steam-rendered, of good color, high steam flavor, and a harder fat than City, but less so than No. 1.

It is rendered by the large slaughtering houses of the West in immense quantities and consists of gut fat and sometimes a little trimming.

Head fat often goes into this lard and the leaf at times may be a constituent. But only when the leaf can not be sold in the form of "neutral" lard for butterine does leaf lard find itself in the Western lard. Some back-bone fat at times may be present. The lard is shipped to the East in tierces and tank cars.

The first sample of No. 1 lard tested gave a decided green color. After further analysis the absence of any vegetable adulteration was pretty conclusively proven, and thinking that this might be a sporadic case only, samples of this grade of lard were obtained from all the firms who were rendering it in the vicinity of New York. On testing, each sample gave an undoubted green coloration, some, however, being more decided than others. After further examination of the lards it was decided that they

| | Hübl figure. | Titre ° C. | Rise of temperature with sulphuric acid, 1° C. | Bechi's silver nitrate test. | Milliau's silver nitrate test. | Welman's phosphomolybdic acid test. | Microscope. | Free fatty acid. Per cent. | Specific gravity, 98° C. 15° C. |
|---|---|---|---|---|---|---|---|---|---|
| 1. | 54.5 | 41.4 | 30.5° | Negative. | Slight discoloration. | Decided green. Blue if alkaline. | Lard only. | ... | ..... |
| 2. | 55.6 | 41.4 | 31.8° | " | " | " " | " | ... | ..... |
| 3. | 58.6 | 40.2 | 34.8° | " | " | " " | " | ... | ..... |
| 4. | 53.7 | 41.4 | 30.0° | " | " | " " | " | 0.73 | 0.8595 |
| 5. | 55.4 | 41.4 | 31.5° | slight discoloration. | " | " " | " | ... | ..... |
| 6. | 56.1 | 41.4 | 31.7° | negative. | " | " " | " | ... | ..... |
| 7. | 47.7 | 42.4 | 25.5° | slight discoloration. | " | " " | " | ... | ..... |
| 8. | 51.7 | 41.8 | 31.5° | negative. | " | " " | slight indication of beef. | ... | ..... |
| 9. | 52.0 | 41.9 | 29.5° | slight discoloration. | " | " " | " " | ... | ..... |
| 10. | 48.9 | ... | ... | ..... | ..... | " " | ..... | ... | ..... |

were pure hog fat. To corroborate the results a sample of the stock from which the lard is rendered was procured and after cleansing, was rendered in the laboratory. The resulting lard gave a decided green coloration with phosphomolybdic acid. The tests made upon nine samples of No. 1 lard and one sample of lard rendered in the laboratory from No. 1 lard stock may be seen in the table. Lards 1 to 9, inclusive, are those obtained

from the renderers. Lard 10 is that rendered in the laboratory.

The iodine-absorption figure was obtained in the usual manner, great care being taken in the manipulation, duplicates being run, blanks carried through with each test, and the flasks in which the determinations were made being furnished with ground-glass stoppers and gutters to hold a solution of potassium iodide seal, to prevent as far as possible any loss of iodine in vapor.

The "titre" is the crystallization temperature of the separated, washed, dried, and filtered fatty acids. The highest point which the mercury reaches, after the rise of temperature due to the liberation of the latent heat has begun, is the temperature recorded.

The rise of temperature with sulphuric acid is of no absolute value as each chemist has his own method of manipulation. The results of the test are simply given for comparison with each other in connection with the corresponding Hübl and "Titre" figures.

The Bechi test was carried out upon the glycerides using an alcoholic solution of silver nitrate. The words "slight discoloration" do not indicate the presence of cottonseed-oil which, in appreciable amounts, produces heavy blackening and often a silver mirror.

The Milliau modification of the Bechi silver nitrate test was carried out upon the fatty acids and the discoloration produced in each case was of a very slight character.

Welman's phosphomolybdic acid test on each sample showed a decided green color and on saturation of the mixture with ammonia the test turned a decided blue. By the words "decided green," in the table is meant, not a greenish yellow tinge, but a green color that was unmistakable to the eye. On the other hand, the tests were not of that deep emerald shade, such as a large percentage of cottonseed-oil would exhibit.

The microscopical examination was carried out upon crystals formed from saturated solutions of the fats in ether and showed in but one case any suspicion of the presence of beef fat, and here, sample 8, the result was doubtful.

The free fatty acid percentage was obtained in the usual way by titration and the use of phenolphthalein as indicator. The result was calculated to oleic acid.

The specific gravity was taken with a Westphal balance, the fat at a temperature of 98° C. being compared with an equal volume of water at 15° C. No correction was made for the expansion of the glass of the bob.

These lards were all hard fats with generally a high steam flavor, but with an inferior color.

It will be seen that there is quite a variation in the Hübl figures of the lards in the table; *viz.*, from 47.7 to 58.6. This is explained on glancing through the next column, when one notices that the titre decreases with approximately the same regularity with which the Hübl increases. The titre is a good guide to the hardness of the fat, that is, to the proportion of liquid to solid glycerides. As the amount of oleic glyceride increases in proportion to the amounts of stearic and palmitic glycerides, the fat becomes softer, the titre test is lower, and consequently, owing to the greater preponderance of unsaturated glyceride, the iodine-absorption figure becomes higher. The lards then owe their difference in Hübl figures to the difference in their fat composition. In the different rendering establishments, the proportion of fats used from different parts of the hog evidently varied. I consider that all the samples consisted of pure hog fat without any cottonseed or other vegetable adulteration. What constituent of this class of lards it is that has the reducing action upon the phosphomolybdic acid, I do not pretend to say. Whether it is a normal product of that portion of the fat of the hog, or simply an impurity introduced or not eliminated in the rendering process, or a peculiarity imparted to the fat at certain seasons of the year, or due to feeding, I am undecided.

Nearly all of the many samples of City lard, both steam and kettle-rendered, tested gave a negative result. In one or two cases, slight green tinges were observed. Of the fifty-seven undoubtedly pure samples tested, each representing on an average 100 tierces of lard, fifty gave no green color and seven gave a slight green tinge.

Western steam lard often gives a slight green test. Of the twenty-nine undoubtedly pure samples tested, each representing on an average 100 tierces, nineteen gave no green and ten a

slight green color. The tests were not as decided as those on the No. 1 lard but still distinctly visible. These results are probably due to the presence of the large percentage of No. 1 lard which the Western lard contains.

I might say further that lard rendered from the leaf alone, which does not, as far as I know, find its way to the lard market in this country, does not give a green color with the reagent. This fact may have been the cause of the many favorable endorsements which appeared after the first publication of the reaction. In order for the chemist to make a fair trial of the reagent, what, apparently, would appear fairer than to obtain a leaf and render it in the laboratory and make tests upon this lard?

In conclusion, I would say, that for the detection of less than ten to fifteen per cent. of cottonseed-oil the test is unreliable, as, in such an instance, no reaction may be produced. When a slight green is the result of a test, the presence of cottonseed-oil is not proven. When a heavy green color, deep emerald in shade, is obtained, the addition of a vegetable oil in considerable amounts is fairly certain. But it is easy to detect such large additions by other methods, and the phosphomolybdic test may be considered to be of slight analytical value and certainly does not fill that long-felt want of a simple test which will reliably indicate small percentages of cottonseed or other vegetable oils in lards.

LABORATORY OF THE CENTRAL LARD COMPANY,
October 29, 1894.

## SOME NEW SOLVENTS FOR PERCHROMIC ACID.[1]

BY WILLIAM M. GROSVENOR, JR.

Received November 8, 1894.

ON the addition of hydrogen peroxide to an aqueous solution of potassium dichromate acidified with sulphuric acid, a blue color is produced, which is supposed to be caused by the formation of perchromic acid. Ether dissolves the blue substance, forming an intensely colored, deep blue solution. On standing, the perchromic acid in this solution decomposes with the formation of chromic acid or salts of chromium.

Recently, Griggi (*J. Chem. Soc.*, **64**, 2,223) has stated that

[1] Read before the New York Section, December 8, 1893.

perchromic acid is also soluble in amyl alcohol, and that this solution is more stable than the ethereal solution, the color lasting for six hours. With a view to studying the behavior of perchromic acid toward certain substances, various organic liquids were tried as solvents for perchromic acid. A two per cent. solution of potassium dichromate was slightly acidified with sulphuric acid and then shaken with the solvent and hydrogen peroxide, after which it was allowed to stand. The following substances failed to dissolve the perchromic acid:

Carbon disulphide, benzene, ligroin, spirits of turpentine, castor oil, oil of wintergreen, oil of bergamot, kerosene, paraffin oils, chloroform, carbon tetrachloride, toluene, nitrobenzene, and aniline.

The following substances were found to be solvents for perchromic acid:

Ethyl acetic ester, valerianic ether, amyl valerianic ester, amyl chloride, amyl butyric ester, amyl formic ester, and amyl acetic ester.

In order to determine which of the solutions of perchromic acid lasted the longest, the following experiments were made. Equal amounts of a dilute solution of chromic acid were shaken in the presence of the solvents with equal amounts of hydrogen peroxide, in small oil-sample bottles, and allowed to stand on a window frame exposed to a strong light. The temperature varied from 10°–20° C. The results were as follows:

Amyl alcohol retained its color one hour and ten minutes, then turned brown.

Amyl chloride retained its color one hour and fifty-five minutes, then turned colorless.

Amyl butyric ester retained its color one hour and fifty-five minutes, then turned brown.

Amyl valerianic ester retained its color two hours and ten minutes, then turned green.

Valerianic ether retained its color two hours and thirty-five minutes, then turned colorless.

Amyl formic ester retained its color sixteen hours and fifty-five minutes, then turned white.

Amyl acetic ester retained its color seventeen hours and fifty-five minutes, then turned colorless.

Ethyl ether retained its color eighteen hours and twenty-five minutes, then turned colorless.

Ethyl acetic ester retained its color twenty-three hours, then turned colorless.

These results do not agree with the observations of Griggi, that the amyl alcohol solution of perchromic acid is more stable than the solution in ether. The most stable solution is that in ethyl acetic ester. The time of duration given by Griggi, six hours, was evidently found under different circumstances. If the layer of the solvent is allowed to remain upon the aqueous layer the decomposition of the perchromic acid is greatly accelerated. The above experiments were made in this manner. Those of Griggi may, perhaps, have been made under other conditions in this respect.

CHEMICAL LABORATORY OF THE BROOKLYN
POLYTECHNIC INSTITUTE.

## SOME FACTS OBSERVED IN THE DETERMINATION OF PHOSPHORIC ACID BY THE MOLYBDIC ACID PROCESS.

BY RUDOLF DE ROODE.

Received November 26, 1894.

THE length of time necessary for the complete precipitation of phosphoric acid seems to be much less than is generally supposed. Portions of the same solution were treated with molybdic solution and allowed to stand at 65° C. for five, ten, fifteen, twenty, thirty, forty, fifty, and sixty minutes, respectively, and two portions stood in a warm place over night. The phosphoric acid determined as usual as magnesium pyrophosphate, showed that the precipitation was complete after standing only five minutes. The weights of magnesium pyrophosphate were as follows:

| | | |
|---|---|---|
| 5 minutes | 0.0676 gram | |
| 10 " | 0.0672 " | |
| 15 " | 0.0674 " | |
| 20 " | 0.0672 " | |
| 30 " | 0.0669 " | Average 0.0673 |
| 40 " | 0.0670 " | |
| 50 " | 0.0673 " | |
| 60 " | 0.0675 " | |
| 12 hours | 0.0671 " | |
| 24 " | 0.0676 " | |

By making a determination of phosphoric acid, using twenty-

five cc. of a very dilute sodium phosphate solution and the same quantities of reagents as are used in a regular determination, and then adding twenty-five cc. of this same dilute sodium phosphate solution to a regular determination and using the first determination as a blank which is subtracted from the last, we get a lower result, which would seem to indicate that a regular determination, without the addition of the phosphate solution and subtraction of the blank, gives too high a result.

A dilute sodium phosphate solution (twenty-five cc.) gave, with the same quantities of reagents as ordinarily used,

| | | | | |
|---|---|---|---|---|
| 1 | 0.0158 | gram of | magnesium | pyrophosphate. |
| 2 | 0.0161 | " | " | " |
| 3 | 0.0156 | " | " | " |
| 4 | 0.0163 | " | " | " |
| 5 | 0.0160 | " | " | " |
| Average | 0.0160 | " | " | " |

Twenty-five cc. of an acid phosphate solution, together with twenty-five cc. of the above sodium phosphate solution and the same quantities of reagents gave

| | | | | |
|---|---|---|---|---|
| | 0.0821 | gram of | magnesium | pyrophosphate. |
| Blank | 0.0160 | " | " | " |
| Difference | 0.0661 | " | " | " |

The average of the ten results obtained where no blank was subtracted was 0.0673 gram magnesium pyrophosphate, making a difference of 0.0012 gram.

Three of the weighed precipitates of magnesium pyrophosphate, in the series of ten, were redissolved in nitric acid, and reprecipitated with molybdic solution and magnesia mixture, ignited in the same crucibles and weighed. At first the magnesium pyrophosphate weighed:

| | |
|---|---|
| 1 | 0.0672 |
| 2 | 0.0670 |
| 3 | 0.0671 |

After solution and reprecipitation:

| | |
|---|---|
| 1 | 0.0660 |
| 2 | 0.0660 |
| 3 | 0.0659 |

Again dissolved and reprecipitated as before:

1 ..... 0.0659
2 ..... 0.0658
3 ..... 0.0657

There seems to be no further loss on reprecipitation, and the results, after the second and third precipitation, agree closely with the results obtained by using and subtracting a blank. These results also would indicate that somewhat too high results are obtained by the regular method for phosphoric acid determination.

Another fact along this same line was also observed; *viz.*, that if different quantities of the same phosphate solution are precipitated, the larger quantity gives the lower and more correct result. Thus, twenty-five and fifty cc. of a phosphate solution, precipitated as usual, gave quantities of magnesium pyrophosphate which, when expressed in percentage of $P_2O_5$, were:

Twenty-five cc. gave 26.05 per cent. and 26.10 per cent.
Fifty cc. gave 25.96 per cent. and 25.97 per cent.

And another solution in like manner:

Twenty-five cc. gave 36.38 per cent.
Fifty cc. gave 36.18 per cent.

The most plausible explanation of this also seems to be that there is some source of error tending to give too high a result, which is multiplied more the smaller the quantity which is taken, and it would seem desirable, for the sake of accuracy, to employ as large a portion as is convenient.

The foregoing experiments seem to warrant the following conclusions:

1. That our present method for determining phosphoric acid seems to give results which are somewhat too high.

2. That the results obtained by using a large quantity of substance, and obtaining large precipitates, are lower and somewhat more accurate than those obtained where smaller quantities are employed.

3. That somewhat lower and more accurate results are obtained by using a blank made by employing a dilute solution of a phosphate, which is added to each determination. This blank, previously determined, being subtracted from the final result.

4. That accurate results, agreeing with those obtained by the

use of the blank, are obtained by redissolving the magnesium pyrophosphate and reprecipitating.

5. That five minutes digestion at 65° C. seems to be sufficient for the complete precipitation of phosphoric acid by molybdic solution.

AGRICULTURAL EXPERIMENT STATION,
MORGANTOWN, WEST VIRGINIA,
November 12, 1894.

## THE ADDITION OF CALCIUM CHLORIDE TO THE SOLUTION OF A FERTILIZER IN THE DETERMINATION OF POTASH.

BY RUDOLF DE ROODE.
Received November 26, 1894.

MR. H. A. HUSTON has proposed the addition of a solution of calcium chloride to the solution of a fertilizer in the determination of potash, in order to furnish sufficient calcium to form tricalcium phosphate with all the phosphoric acid present, and thereby permit of the use of platinum dishes in the Lindo-Gladding method. In testing this proposition I find that when sufficient calcium chloride was added to combine with all the phosphoric acid present and then ammonia added in excess and a portion of the solution filtered off, no test for phosphoric acid could be obtained. But, that if in addition to the calcium chloride and ammonia, some ammonium oxalate or carbonate was added, a filtered portion of the solution *did* give a test for phosphoric acid. This is accounted for by the fact that the calcium phosphate, which was precipitated by the ammonia, is changed by the ammonium oxalate or carbonate into calcium oxalate or carbonate and ammonium phosphate, so that the very object for which the calcium chloride was added is defeated by the addition of the ammonium oxalate or carbonate In order to make the use of calcium chloride effective it is necessary to filter off from the precipitate formed by the calcium chloride and ammonia and to then add the ammonium oxalate or carbonate to the filtrate. This necessitates two separate filtrations, and it is doubtful if we have in Mr. Huston's suggestion anything better than, or even so good as in the present alternate method.

AGRICULTURAL EXPERIMENT STATION,
MORGANTOWN, WEST VIRGINIA,
November 12, 1894.

## ON THE PREPARATION OF AMMONIUM CITRATE SOLUTION.

By Rudolf de Roode.

Received November 26, 1894.

MANY times in preparing a solution of ammonium citrate, I have observed a fact which seems to indicate that the preparation of a strictly neutral solution is an extremely simple matter. If some citric acid is treated with ten per cent. ammonia until dissolved, the solution becomes quite hot, and if it is now diluted to nearly the proper specific gravity, made decidedly alkaline with ammonia, and allowed to stand over night in an open dish, it will be found in the morning to be strictly neutral.

Being warm and in an open dish the excess of ammonia escapes completely, leaving it neutral. For the last four or five times which I have had occasion to prepare an ammonium citrate solution, I have observed this fact and each time have found it unnecessary to alter the neutrality in the least degree. I find it very convenient. I also find it advantageous to add a small quantity of salicylic acid to the solution (about one gr. for five liters of solution is sufficient). This is added before neutralization, so that the salicylic acid is also neutralized by the ammonia. The salicylic acid prevents the growth of fungus in the solution and it remains unchanged a long time. Some solution six months old when used in fertilizer work, gave results practically identical with those obtained by the use of a freshly prepared solution.

Agricultural Experiment Station,
Morgantown, West Virginia,
November 12, 1894.

## THE DETERMINATION OF POTASH IN MANURES.

By W. E. Garrigues.

Received November 15, 1894.

THE following method for the determination of potash in fertilizers, has been in use in the writer's laboratory for some months, and in view of its ease, quickness, and comparative accuracy is believed to be a decided improvement on that of Lindo-Gladding.

It depends upon: 1. The ignition of the material with sul-

phuric acid, thereby converting all potash present, to sulphate, if not already in that form, and at the same time expelling any ammonia and organic matter. 2. Precipitation of the sulphuric acid with barium chloride. 3. Precipitation of the excess of barium, together with other earthy bases, by sodium carbonate. 4. Evaporation of the filtrate with platinic chloride as usual.

The process entails but one filtration and evaporation and with due precaution the final precipitate of potassium platinochloride is obtained practically chemically pure.

The analysis: Ten grams of the sample are weighed into a platinum dish and worked into a paste with concentrated sulphuric acid. The rod is wiped with a small piece of filter paper, which is added to the sample, and the whole ignited, raising the heat gradually and finishing with a blast until the residue is white, or red if much iron be present.

The contents of the dish are now scraped out into a porcelain mortar and ground to a fine powder, a little hot water is added, washing out the dish at the same time, and the mass triturated for a few minutes. It is next washed into a 500 cc. flask and boiled with 250 cc. of water for half an hour, when a ten per cent. solution of barium chloride is run in five cc. at a time and boiling after each addition, until no further precipitation is visible.

Add a single drop of phenolphthalein solution and sodium carbonate, drop by drop, until a faint permanent rose color is obtained. Boil for a minute, set aside to cool, and make up to the mark. Filter through a dry paper and measure out fifty cc. of the filtrate = one gram of sample. Add hydrochloric acid to slight acid reaction, as shown by the disappearance of the rose color, and evaporate on a water-bath with platinic chloride. Wash the precipitate with alcohol, sp. gr. 0.848 (= eighty per cent. by weight), dry at 100° C., and weigh. For potash salts, the ignition with sulphuric acid is omitted.

Remarks: 1. The sulphuric acid must be added cautiously as fertilizers containing chlorides and nitrates react somewhat violently, endangering loss of the assay. 2. It is important that the ignited mass be very finely pulverized, otherwise the calcium sulphate, most of which remains insoluble, will mechanically enclose the potassium sulphate and prevent its complete

solution. 3. An excess of sodium carbonate is not permissible as double decomposition with the precipitated barium sulphate may take place, leaving sodium sulphate in solution and rendering erroneously high results. 4. It is recommended to turn the flame under the bath below boiling temperature when the solution has evaporated to small bulk. In case it then goes to hard dryness, no harm is done, while, if the bath be boiling, it is necessary to keep a close watch lest this occur. 5. For the filtration and weighing, a Gooch crucible, fitted with a single disk of filter paper, leaves nothing to be desired.

This method was first adopted as a safe one, on its favorable showing when checked against the Lindo-Gladding, and has since proven in the writer's hands very much more concordant than the latter. Since the publication of Mr. Norman Robinson's criticism of several well-known methods of potash determination (This JOURNAL, **16,** 364), the writer has made a more careful investigation of the value of this process, comparing it with two others and incidentally confirming some of Mr. Robinson's work.

It was thought most satisfactory to operate on samples of known composition, and with this end in view several, representing the usual variety met with in commerce, were prepared. In each case the potash "occluded" by the various precipitates was determined after washing until no reaction with silver nitrate was visible. To facilitate comparison all the figures are given in per cent. potassium oxide.

| Nature of Sample. | Calculated content potassium oxide. | Found by Lindo-Gladding. | Recovered from precipitates. | Found by Stassfurt. | Recovered from precipitates. | Found by Garrigues. | Recovered from precipitates. |
|---|---|---|---|---|---|---|---|
| Complete Fertilizer; containing $K_2SO_4$. | 5.40 | 5.16 | 0.20 | | | 5.17 | 0.09 |
| | | 5.28 | 0.11 | | | 5.19 | 0.12 |
| | | | | | | 5.25 | 0.09 |
| | | | | | | 5.28 | 0.17 |
| Complete Fertilizer containing KCl. | 6.31 | 6.12 | 0.15 | | | 6.22 | 0.08 |
| | | 6.09 | 0.14 | | | 6.14 | 0.12 |
| Mixed salts $KCl+CaCl_2+MgSO_4$. | 63.17 | 63.19 | 0.12 | 62.85 | 0.19 | 62.75 | 0.18 |
| | | 62.74 | 0.15 | 62.80 | 0.17 | 62.95 | 0.15 |

12-27-94

The figures under the headings of the three methods do not include the per cent. recovered from precipitates. In the Stassfurt method the quantity of barium chloride necessary was calculated and exactly added, so that no doubt need exist as to the potassium platinochloride obtained having been contaminated with sulphates on an excess of barium chloride. In one case the total return by the Lindo-Gladding method was apparently more than was present, due no doubt to a slight contamination with calcium sulphate. It should be remarked that no corrections were made for the volume occupied by the precipitates in the flasks. The factor used in calculating the double chloride to potassium oxide was 0.193.

The writer is frank to acknowledge that frequently the Lindo-Gladding method has given him very discordant results. This has been especially noticeable in fertilizers containing liberal amounts of potash. An aggravated case of the kind was a return in triplicate of 10.16–11.37–12.75. The writer's method gave 12.73–12.76 and an experiment station working on the same sample found 13.10. Two other instances of disagreeing duplicates by the Lindo-Gladding process are 4.76–5.07, and 6.10–6.54.

It is difficult to give any satisfactory reason for these discrepancies, as they are probably due to a multiplicity of causes. The writer has always felt the re-solution of the ignited potassium sulphate in water to be an unsatisfactory step and this alone sufficed to make the adoption of a new method desirable to him, the official alternate method being too tedious for ordinary use.

It is suggested that the material differences among chemists working by the Lindo-Gladding method, may be, in part, due to the varying strength of the alcohol-wash. The official directions, though they mention eighty per cent., do not lay sufficient stress on this point. If ninety, or even eighty-seven, be used in the second washing, ammonium chloride is precipitated with consequently higher returns.

In conclusion, while it is plain the method here proposed does not, in common with those now in use, return quite all the potash, it is seemingly less accurate than none and certainly less discordant than the Lindo-Gladding, besides being more satis-

factory to work, and quicker. It obviates the no small difficulty of precipitating all the sulphuric acid without adding an excess of barium chloride in the Stassfurt, and avoids the tedious evaporations and filtrations entailed by the alternate. Against all these advantages there has appeared so far only one disadvantage: the necessity of using a greater quantity of platinic chloride.

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## THE RAPID AND ACCURATE ANALYSIS OF BONE-BLACK.[1]

By W. D. Horne, Ph.D.

SEVERAL years' experience in the analysis of bone-black have led me to the adoption of the following method for attaining accurate results with comparative rapidity.

In new char, bought from the dealer, the determination of moisture is of importance, being frequently limited by contract to three per cent.

In char, in constant use in sugar refineries, the moisture in the revivified sample is of no importance under usual conditions.

The moisture is determined by heating two grams of the unground char for two hours in a hot air-bath at 140° C. It can be weighed between watch-glasses held by a clip to prevent absorption of moisture.

A convenient way of estimating calcium carbonate is with Lunge's nitrometer, using mercury. Two grams of the finely pulverized sample are introduced into a two-ounce Erlenmeyer flask and moistened with three cc. of a saturated solution of mercuric chloride, the tube of ten cc. of hydrochloric acid (sp. gr. = 1.12) introduced and the flask closed with a rubber stopper, which, with a short glass tube and a rubber tube, is hung to the tube of the three-way cock. By tipping the acid out upon the char and properly manipulating the stop-cock the carbon dioxide is liberated, collected, and measured. Any hydrogen sulphide given off is absorbed by the mercuric chloride. Corrections are made for temperature and atmospheric pressure.

For the determination of carbon, iron, calcium sulphate, and insoluble ash, one portion is used. In preparing the sample

[1] Read before the New York Section, November 9, 1894.

for analysis the iron particles must first be removed by a magnet and the char then ground to an almost impalpable powder.

Two grams of this are moistened with water and treated in a four-ounce covered beaker, with twenty cc. hydrochloric acid, and boiled gently until solution is complete, which is within thirty minutes. The beaker is filled up with boiling water and after settling, which takes place almost immediately, decanted upon a weighed platinum Gooch crucible with asbestos plug. The carbon is washed by decantation in this way five or six times, until the filtrate is free from chlorine. The original filtrate and first decanted washing contain practically all of the iron and calcium sulphate. The following wash-waters can usually be rejected. The carbon is washed out of the beaker into the Gooch, and is then washed with eighty per cent. alcohol, ninety-five per cent. alcohol and ether, each two or three times, set in a water-jacketed air-bath, and heated at 100° C. to a constant weight, which will take about three hours. The increased weight is due to carbon and ash. The carbon is burned off over the blast. The loss of weight is then carbon, and the difference is ash.

To the acid solution containing iron and calcium sulphate a drop of methyl orange solution is added and ammonia to nearly neutral reaction. Ammonium acetate is added until the solution turns yellow and then a few drops in excess. The solution is now heated below 70° C. until complete precipitation of iron and aluminum phosphate takes place, which is usually in about twenty minutes. The precipitate, after being washed free from chlorides, is dissolved by dilute sulphuric acid into a six-ounce Erlenmeyer flask, ten cc. of a ten per cent. solution of sodium sulphite added, and boiled to reduce the iron and to expel the sulphur dioxide. To ascertain when this gas ceases to come over, the vapor is led from the flask through a glass tube fitting through the rubber stopper and inclining vertically downward at its outer end. Under this is held a test-tube of dilute potassium permanganate acidified with sulphuric acid. So long as sulphur dioxide, issues it will decolorize the permanganate solution in the tube when the gas is caused to bubble up through the upper half inch of the solution. When the sulphur dioxide

is all out a drop of the solution from the flask is tested with potassium sulphocyanide for ferric iron. When the reduction is complete the solution is cooled and titrated with permanganate. If alumina is to be determined the above-mentioned precipitate of the iron and aluminum phosphates can be treated with 150 cc. of ammonium molybdate solution, to precipitate the phosphoric acid, and filtered. In the filtrate iron and alumina are precipitated as hydroxides by ammonia, filtered off, dissolved in hydrochloric acid, reprecipitated with ammonia, collected, ignited, and weighed. The two may then be separated by any of the well-known methods.

The filtrate from the iron and alumina precipitation contains the calcium sulphate. This solution is acidified with hydrochloric acid, and barium chloride added to precipitate the sulphuric acid. The barium sulphate is treated in the usual way and calculated to calcium sulphate.

Calcium sulphide may be determined by treating five grams of char with twenty cc. of nitric acid and evaporating nearly dry, adding twenty cc. of hydrochloric acid, and evaporating again very low to expel nitric acid, taking up in hydrochloric acid, and in an aliquot portion of the filtered solution precipitating the sulphuric acid in the usual way with barium chloride. From the weight of barium sulphate found, is deducted that found as above, due to calcium sulphate. The remainder is that due to calcium sulphide.

The physical condition of the char is of great importance and should be thoroughly examined into. The grist is estimated by throwing 100 grams upon a sieve of known mesh, shaking gently, and weighing what passes through. This portion may, in turn, be passed through successively finer sieves, and weighed after each. In shaking, the sieve should be tapped only very gently—otherwise particles of char will be forced through which, correctly, belong above.

To determine the density of the char it should be carefully filled into a weighed flask of 50 or 100 cc. capacity, and of very gently sloping sides. Admitted into such a flask through a funnel the char fills it completely without leaving vacant recesses at the shoulders. This is weighed, from which is cal-

culated the specific gravity of the char when loose and the pounds per cubic foot. Now the flask is tapped lightly on the table and as the char settles down more is added until no further settling takes place, and the flask is filled to the mark. This gives the weight of char when packed, from which may be calculated, as before, the specific gravity and weight per cubic foot.

As char grows old in use its porosity decreases and its specific gravity increases. It is sometimes desirable to know its porosity. To do this the weighed flask is filled with distilled water, the char introduced, little by little, displacing part of the water from the flask. At the same time the water remaining displaces from the char its contained air, which rises in minute bubbles. The flask is tapped to pack the char, and, when filled to the mark, is heated on the water-bath to expel all air. After cooling, the supernatant water is removed and the flask and contents weighed. The increased weight over that of the flask packed with char is that of the contained water, from which can be calculated the capacity of the char for any liquid of known specific gravity.

The repeated handling which bone-black receives in continued use in sugar refineries, etc., tells on it very seriously, as the friction of the grains against each other and the machinery wears it into dust. This change is slow, but in the long run is very costly, as the fine dust has to be discarded and replaced by new char.

Any method, therefore, which would enable one to judge of the relative durability of samples of char under this continued friction should be worthy of consideration. I have attempted to contrive such a test, and after a good many experiments have found one which promises well. Twenty-five grams of the char to be tested, between sixteen and twenty-four grist, approximately, are thrown on a sieve with circular holes, one-fiftieth of an inch in diameter, the sieve shaken back and forth ten times, tapped three times, and the shaking and tapping repeated twice. This drives the dust through, and it is weighed. Dust and char are then both put into a cylinder of tinned iron, four inches in diameter, and two inches deep; then six glazed porcelain marbles five-sixths of an inch in diameter and weighing together 74.66 grams are added. Now the can is shaken back and forth

with slightly rotary motion 200 times, the marbles removed, and the char sifted as before. The increased weight of dust is calculated to per cent. of the char used. These tests are pretty constant for different portions of the same sample of char.

The dust formed thus from a good new char was in three cases 1.72 per cent., 1.46 per cent., and 1.76 per cent. From another new char 2.68 per cent. and 2.44 per cent. Two grades made by one firm gave 2.16 per cent. and 2.16 per cent. in one case, and 2.86 per cent. and 2.87 per cent. in the other. Char which had been in use ten months and whose softer parts had already been separated by use gave 0.92 per cent. and 0.94 per cent., showing that it was then in a better wearing condition than when it first entered into use.

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## THE ASPHALT QUESTION.

By S. F. Peckham.

THERE has lately been published some very interesting reading concerning this question. To go back a few months, in October, 1892, Consul Pierce made a report that seemed to leave very little to be said in reference to Trinidad asphaltum from any standpoint. A few months later, Mr. Clifford Richardson published in the *Journal of Analytical and Applied Chemistry*, for Dec. *1892*, and Jan. *1893*, a paper in which he embodied the results of a most elaborate series of technical analyses of Trinidad asphalts. Within the last twelve months there has been published a voluminous report on Trinidad asphalt by Mr. Richardson, in the "Mineral Resources of the United States." In several late numbers of *Paving*, Mr. D. Torrey has shown that a method of analysis of asphalts may be based on successive solutions in alcohol; and he has also discussed in a very suggestive and intelligent manner, the general subject. In the July number of *Paving*, Messrs. Richardson and Bowen pay their respects to the report of Messrs. Leffman and Sadtler, made to the Citizens' Municipal Association and Trades League, of Philadelphia. In the August number of the same journal Messrs. Leffman and Sadtler reply to their critics. In the December number of this Journal Miss Laura Linton publishes a paper, in which she gives the result of a very careful

research upon the methods heretofore employed in the technical analysis of asphalts. I am also just in receipt of a report upon "The Gas and Petroleum Yielding Formations of the Central Valley of California," by W. L. Watts, of the State Mining Bureau.

I propose, by a general review of these papers, to ascertain where a chemist, who is occasionally consulted in reference to asphalt, might reasonably take his stand.

It is now about fifty years since I first noticed, in a number of the *Penny Magazine*, an illustrated article on the "Pitch Lake of Trinidad." My interest in this wonderful phenomenon has never abated. Somewhere late in the fifties, when the Downer Kerosene Oil Co., was ransacking everywhere, but in Pennsylvania, for crude material for illuminating oil that was cheaper than Boghead Mineral, or Albertite, the late William Attwood was sent to Trinidad, where he remained two or three years. Several years after his return it was my good fortune to meet him, and I listened with eager interest to his description of the so-called lake, which he represented as a mass of asphaltum of unknown depth, floating upon a veritable lake of water. His experiments in the line of preparing illuminating oil from the asphalt were so far from a success that the late Samuel Downer once facetiously remarked, that the Trinidad pitch was, without doubt, derived from right-whales, black-fish, etc., while Pennsylvania petroleum was certainly nearly pure sperm oil. Later investigations have shown that both Mr. Attwood and Mr. Downer were considerably mistaken in their conclusions.

The report of Consul Pierce shows that the so-called pitch lake has no definite boundaries, but overflows towards the sea, over the rim of its irregularly circular basin, on one side. His report also shows that the sources from which the bitumen rises to the surface, are not confined to the strata beneath the so-called pitch lake, but are also found in the strata that underlie that portion of the island of Trinidad adjacent to the lake, to such an extent that unknown areas are covered with masses of asphalt, of unknown thickness. This asphalt, from both inside and outside the lake, was mined and sold, but that from outside the lake was finally distinguished as "land asphalt" by those who chose to

do so. Consul Pierce shows conclusively that the same cosmical forces that bring asphaltum to the surface in large quantity at the lake, bring it to the surface at many other points upon the island in smaller quantity, and, that other things being equal, the asphaltum is the same thing in both instances.

In Mr. Richardson's elaborate paper above referred to,[1] he gives results of analyses of a number of specimens that were taken from the lake, and compares them with corresponding results of analyses of a number of specimens taken from the land. He admits that no practical difference can be shown to exist between good commercial samples from either source; but he insists on introducing analyses of lake asphalt that are too soft for commercial purposes, and also of a lot of land specimens that, so far as serving any useful purposes are concerned, are neither more nor less than rubbish. No one familiar with deposits of surface asphalt in Southern California, would visit an asphalt bed and dignify the refuse from the numerous fires that, from immemorial periods, have swept over its surface, with the names of "iron-pitch," etc., and think an argument necessary to prove that the ashes, cinders, coke, and half-burned asphaltum, are unfit for street pavement. I have seen masses of coke, from fifteen to eighteen inches thick, taken from burnt asphalt beds, and thousands of tons of melted and half-burned asphaltum, in streams miles in length, the analysis of which would afford most convincing proof that they were unsuitable for street pavement. Setting aside the soft pitch on the one hand, and the rubbish on the other, it appears to me, that any unprejudiced person must admit, that Mr. Richardson's paper proves either too little or too much; either that the methods and material he used proves nothing, as is really the case, or that the results he has obtained prove the practical identity of "lake" and "land" asphalt of good commercial quality.

In the report by Mr. Richardson in "Mineral Resources of the United States for 1893," he goes into the history of the paving industry, and gives some very interesting details, both political and commercial, the argument of which appears to be that while there are other asphalt paving materials to be had in the

1. *J. Anal. Appl. Chem.*, Dec. *1892*, and Jan. *1893*.

world, the only material worth considering is that laid by the Barber Asphalt Paving Co., that use and practically own the "lake" deposit, which, after all, is not a lake at all, but fills "the crater of an old mud volcano." He says, "in times past it appears that the continued welling up of pitch at the center of the lake filled the crater and caused it to overflow towards the sea." Here again, he either proves that the whole of the pitch is worthless, or that the whole deposit outside and inside the crater is practically one and the same thing.

He starts into the discussion of the Technology of Trinidad asphalt pavements, with the important information that "The crude pitch is shipped from La Brea in Trinidad in both sailing vessels and steamers." Farther on, he shows by a sort of historical résumé, that a little more care has lately been taken in refining the pitch than formerly, by which the damage resulting from prolonged overheating is avoided to some extent. He then grapples with the cement problem. He says of the fluxing oil, "it should not contain large amounts of hard paraffins, for in this case, while it may be of suitable nature for making cement at ordinary temperatures, it is susceptible to changes and makes the resulting cement too brittle at low temperature and too soft in heat of hot summer sun. The more the oil is of a vaseline nature the better it is. While the oil now in use is a great advance over that of some years ago, there still seems to be room for improvement. "The character of an oil may be learned by determining—

1. Specific gravity.
2. Flash-point.
3. Percentage volatile in seven hours at 400° F.
4. Susceptibility to changes in temperature as revealed in changes in viscosity.
5. Presence of crystals of paraffin scale.

Before mixing, the asphalt is raised to a temperature of 300° F., or thereabout, and to produce rapidly a smooth mixture, the oil should be heated as hot as is convenient. The oil is then pumped or in other ways added to the still, and the mixture agitated for several hours with a current of air until it is quite homogeneous. This agitation must be done with great thor-

oughness to insure a uniform cement, and must be continued whenever the material is in a melted condition, as a certain amount of separation takes place when the melted cement stands at rest. It is, therefore, customary to agitate it constantly with an air-blast when in use as well as in its preparation."[1]

Then he goes on to describe the ingenious toy with which Prof. Bowen, of Columbia College, amuses himself. This instrument is so delicate that, "as the needle (a cambric needle) is not at a normal temperature an allowance must be made." Comment is unnecessary.

In a paper that I read at the Congress of Chemists,[2] held at the Columbian Exposition, I took the position that the residuum in use for softening asphalt that is made from petroleums consisting of paraffins, and that consequently contains paraffins, is not a solvent for asphaltum, and therefore is not a suitable material for an asphaltic flux; as when an attempt is made to incorporate the two materials, the result is a mechanical mixture and not a chemical union as it should be. I based my argument on the results of laboratory experiments, and I now gladly welcome Mr. Richardson to my side, as his very emphatic statements are based upon the much stronger proof of practical experience. In the paper above referred to I further maintained that the custom of "blowing" asphalt, or mixing it by the use of a current of air injected into the molten mass while heated to a high temperature, is all wrong.

Mr. Richardson writes well, and he uses the word "scientific" in a way that sounds well; but I hazard the opinion, that if he read more and wrote less, his opinions would have more weight. The first "scientific" paper in which the effect of the prolonged heating of bitumens was discussed, was published by Boussingault in 1837. He says,[3] "after different experiments, the means that I have finally employed in order to free the bitumen of its volatile principles, consists in exposing it at a temperature of about 250° (C. = 480° F.?) in a Gay-Lussac oil-bath until it no longer loses weight. This method is prolonged, as it is necessary to heat during forty-five to fifty hours, even when operating

[1] Mineral Resources of the United States, *1893*, 651.
[2] *Am. J. Sci.*, Jan., *1894*; *Paving and Municipal Engineering*, Aug., *1894*.
[3] *Ann. chim. phys.*, **64**, 141.

on only two grams of material." In a note he adds, "By this method it is impossible to determine the two principles of the bitumen, as at that temperature a part of the petrolene is oxidized and passes to the solid state or asphaltene." Technologists in petroleum have known for years that prolonged heating will convert paraffin petroleums into a solid residuum. It has also been known for years that California petroleums can be so manipulated by heat as to convert a large percentage of them into an asphaltic residuum, that will contain varying proportions of material soluble in petroleum ether, carbon disulphide, and chloroform, leaving a residue of coke, according to the temperature to which it has been heated. The percentage of material soluble only in chloroform increases also in proportion to the time during which it has been heated. A patent has lately been issued from the U. S. Patent Office for a method or process for preparing these residues.

It seems incredible, that the scientific adviser of a great corporation, that has the reputation of seeking to control the asphalt paving business of the United States, should be ignorant of these facts. Why then this space occupied in the Mineral Resources of the United States, with descriptions of technological processes, that all of the knowledge possessed by the scientific world for the last sixty years, condemns as unscientific?

Mr. Richardson has taken great pains to show that he found a good quality of "land asphalt," that contained, if I remember his figures, two per cent. less of matter soluble in petroleum ether than a fair quality of "lake asphalt." This difference he regards as absolutely exclusive of "land asphalt" for paving purposes. He then describes how this "lake asphalt" is refined. He does not say whether refined lake and land alsphalt differ by two per cent. of matter soluble in petroleum ether or not. He then shows how the refined lake asphalt is softened with a material that, according to his own showing, will not form even a mechanical mixture with the melted asphalt except by constant agitation with a current of air, and that, up to the point when the so-called cement is put into its final resting place upon the street. It is a fair question, whether lake asphalt after this wholly unscientific treatment does not contain a larger percentage of matter insolu-

ble in petroleum ether than would land asphalt, when properly manipulated.

Mr. Richardson says, " Washington has had more experience with sheet asphalt pavements and more time and attention have been devoted to both the scientific and practical sides of the industry there than in any other city in the country."[1] If Mr. Richardson has faithfully represented the state of the art in this highly favored city, in what condition must the rest of the country be found where scientific principles have not been introduced into the industry?

Mr. Richardson has been giving his attention to the scientific principles underlying this industry for a number of years. I think it may be safely said that he has had a better opportunity to become an acknowledged scientific authority upon this subject than any chemist living. After what manner has he used this opportunity? He has published a large number of so-called analyses of asphaltum. When making these analyses he either found a method already in use, which his experience proved to be satisfactory, or he invented a better one. In either case, by long continued use, he made the method his own. I am not aware that he has anywhere described his method of analysis, but the terms in which he has stated the results of his analyses, indicate his method with sufficient clearness. He states the amount of water, the percentage soluble in petroleum ether, the percentage soluble in carbon disulphide, the percentage of organic matter not bitumen, and the percentage of inorganic or mineral matter. It is a fair assumption that with Mr. Richardson's opportunities, he thoroughly investigated every step in this process of analysis, and is prepared to show that water, and not volatile oils or gases, are determined as water; that either petroleum ether of any sp. gr., *e. g.*, any light distillate of petroleum can be used in place of any other, with the same results, or that a distillate of a particular sp. gr., obtained from a particular petroleum should be used. It is further to be presumed, that he is able to show that petroleum ether is the best liquid that can be used for this purpose, and that the separation made by its use is sharp and clearly defined. It is further to be

[1] Mineral Resources of the United States, *1893*, 653.

presumed, that when this residue from which petroleum ether has made a complete solution, is subjected to the action of carbon disulphide, that setting aside the difficulty of obtaining the reagent pure, its action is attended with no serious objections and is complete; that is, it dissolves every trace of bitumen remaining in the residue. All of this should have been proved beyond question years ago. But Mr. Richardson has apparently allowed that two per cent. of difference between lake and land asphalt to so obscure his mental vision that he has left it to the careful and painstaking accuracy of Miss Linton to show that carbon disulphide will not dissolve completely the bitumen from asphaltum, and that boiling spirits of turpentine is an equivalent for carbon disulphide, and is a much more convenient and satisfactory reagent to use.[1]

There are mistakes to which every one is liable and that are properly to be excused; there are others that are absolutely without excuse. I confess, that to my mind, there is no excuse for a man, who, occupying the position or responsibility that Mr. Richardson has occupied, publishes the results of analyses year after year, upon which, as a basis, it has been sought to influence the expenditure of millions of public money, when, in reality, he has made no proper investigation of his processes, and knows nothing respecting the accuracy or proper significance of his results. Mr. Richardson has no right to complain if his constituency hereafter repudiate all of the dicta that he has with, I had almost said, unpardonable arrogance thrust upon the public, in reference to the "Asphalt Question."

I have read the articles of Mr. Torrey with a great deal of interest.[2] They are suggestive. I have not found, by experience, that his method of analysis by solution in alcohol, promises any superiority over that proposed by Miss Linton. The test of a method of analysis is, other things being equal, the parallelism shown in the results when duplicate analyses are made, side by side. In one instance, with her process, I have obtained results parallel to the third place of decimals. Such close correspondence in work of this kind is not generally to be expected;

[1] This JOURNAL, **16**, 809.

[2] *Paving and Municipal Engineering*, Nov., *1893*; April, May, and September, *1894*.

but the process, on the whole, has given me very satisfactory results, and the possibility of rejecting altogether the use of carbon disulphide is a great gain.

Messrs. Sadtler and Whitfield, remark in their article in *Paving*, "While some of the European asphaltic limestones are capable of being used for paving without addition of fluxing material, they have not been found to make as satisfactory pavement as those containing a siliceous base."[1] Why should they? Is not any form of calcium carbonate easily dissolved by rainwater or decomposed by weak acids, such as abound in the street gutters? Will Mr. Richardson please explain why pulverized limestone is required as an ingredient of the asphalt surface used in Washington? Why is it any better than the same amount of fine quartz sand? The reasons given above are sufficient reasons why it is not as good. In California, infusorial earth occurs in many localities in close proximity to deposits of asphalt. It is found to be a very superior material with which to temper asphalt.

On page 52 of the Report of the California State Mining Bureau, above referred to, an extract appears from the Records of the Standard Asphalt Co. There an attempt is made to compare some of Mr. Richardson's analyses of Trinidad asphalt, made with petroleum ether, with other analyses made by G. Q. Simmons, who analyzed California asphalt by using common ether. Other tests are given, made by H. Stillman, who used presumably petroleum ether from California petroleum. Miss Linton has shown that the solvent powers of these three reagents, when applied to the same asphaltum, vary widely; hence they can not be used interchangeably, and results based upon their use can not be compared. The material used should be petroleum ether of sp. gr. 700 equal to 70° B., obtained from petroleum consisting of hydrocarbons of the marsh-gas series—in other words "paraffins."

These criticisms have not been made at the suggestion of, or in the interest of any party to the asphalt question.

UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.,
October 30, 1894.

[1] Ibid. September, *1894*, 120.

## QUICK ESTIMATION OF STARCH.

By P. L. Hibbard.

Received November 3, 1894.

THE accurate estimation of starch in presence of crude cellulose or similar substances containing other carbohydrates soluble in hot water or boiling dilute acids, has not yet been accomplished. Lintner's process of heating in closed vessels under high pressure, with water or a weak acid, like tartaric, *e. g.*, is good when soluble convertible carbohydrates other than starch are absent. Märcker's process of dissolving the starch out of the fiber by means of diastase is also fairly satisfactory. But both methods will bring into solution more or less of the various gums, etc., which are nearly always present in starch-bearing material. Entirely to avoid solution of these bodies is, so far, impossible ; but it is certain that the less the material is heated with water, or especially with acid, the less will they be dissolved. Perhaps the best method published is Märcker's. The substance is boiled with water a few minutes to gelatinize starch, then cooled to 60° C., some diastase added, and the whole heated on the water-bath at 65° C. for one hour, to hydrolyze the starch. The solution is then filtered from the insoluble residue and converted by hydrochloric acid to dextrose, which is then determined by Fehling's solution. All the directions that I have seen, say the mixture must be heated with diastase for one hour, and then it must be heated two or three hours on a water-bath, with a reflux condenser. A modification of this method consists in heating the substance under pressure of three atmospheres, with lactic or tartaric acid, after the first treatment with diastase. The acid is then neutralized and the whole again warmed with diastase. The conversion to dextrose is as before stated. These methods are somewhat long and tedious, besides being liable to bring into solution other bodies than starch, which, by the subsequent process, will reduce Fehling solution.

Whole corn, soaked a few minutes, was stripped of its hulls. These hulls were carefully examined to see that they were free from starch and were not colored by solution of iodine. After

boiling them a few minutes with water, the solution was filtered off and heated with acid a short time. It then reduced Fehling solution somewhat. This experiment shows that mere boiling with water brought into solution some body, which was converted by acid into a reducing sugar.

Having occasion to estimate starch in residues containing much of other soluble carbohydrates, I have modified the method using diastase, so that it is much shorter and easier, as well as fairly accurate. The method is satisfactory for factory work, where great accuracy is not so necessary as speed; and slightly modified is the most accurate method known.

Instead of taking trouble to prepare diastase by precipitating and washing with alcohol, I make a water extract of malt, which answers well. The coarsely pulverized dry malt is covered with water containing fifteen to twenty per cent. of alcohol. After a few hours the infusion is filtered off and is ready for use. The sugar in this must be determined by treating with acid as described below, in order to make the correction due to it when used to dissolve starch. The alcohol to some extent prevents action of the diastase on the starch of the malt, but is chiefly useful to preserve the malt extract, which would ferment very soon if some antiseptic were not present. Twenty per cent. of alcohol will preserve it for two weeks, even in very warm weather. I have found no effective preservative, except alcohol, that does not destroy the diastatic power of the malt extract.

The substance in which starch is to be determined should be finely pulverized, in order that the starch may be easily extracted without long boiling. Enough of the material to contain at least half a gram of starch is placed in a flask with about fifty cc. of water and one or two cc. of malt extract added. The mixture is at once heated to boiling, with frequent shaking to prevent formation of clots of starch. The addition of diastase before gelatinizing the starch, helps to prevent formation of insoluble clots, as it acts above the temperature at which starch becomes pasty. But if the material contains little starch in presence of much fibrous material, there is no particular gain in adding malt before heating to boiling, as

most of the diastase is destroyed by the high temperature, before it has time to act on the starch. After boiling a minute the mixture is cooled to 50°–60° C., and two to three cc. malt extract added. Then it is heated slowly from ten to fifteen minutes till boiling, again partially cooled, and tested with iodine solution. If there is blue, the treatment with malt must be repeated. When all the starch is changed, the mixture is cooled, made up to definite volume, and filtered. I have found fine muslin or linen a very satisfactory filter for this purpose. Though it does not at first filter quite so clear as paper, it is more rapid, not being so easily clogged when the substance is albuminous. The cloth retains all the fibrous material, which might give rise to sugar in the subsequent treatment with acid. An aliquot part of the filtrate, sufficient to contain two or three-tenths of a gram of starch, is placed in a 100 cc. flask with five cc. HCl containing thirty per cent. of acid gas, and water to make about sixty cc. total. This is boiled moderately thirty minutes actual boiling, on a sand-bath. This gives complete conversion. I use a sand-bath and no condenser, as the amount evaporated from a narrow-necked flask in this time is not enough to make much difference. If a water-bath is used longer time is required. The solution is now cooled, nearly neutralized with sodium hydroxide, and the dextrose determined by Fehling solution. With pure starch the solutions obtained are almost colorless, but if the substance contains much albuminoid matter, which will be destroyed by the acid, the solution will be brownish. There is no apparent destruction of sugar in this length of time.

The action of various acids on starch has been investigated by F. Salomon, (*J. prakt. Chem.*, **28,** 82,) and it is concluded that hydrochloric is the best acid to use in the hydrolysis of starch. Less than an hour of moderate boiling with the strength of acid above given is sufficient to convert starch directly without previous solution with diastase. Much longer heating destroys sugar and the solution becomes brown.

The residue left after treatment of a good quality of starch by this method is little, but some of it is soluble in dilute acid, so that direct conversion with acid gives a little higher figures, but

it seems probable that this is largely due to other bodies than starch. I have made many experiments to determine the proper time and best strength of solutions, and find the above given most satisfactory.

This method is simple, rapid, and fairly accurate. A determination of starch may be easily finished in less than two hours. Particular points are: prevention of insoluble clots by addition of malt before heating; the rapid heating prevents any lactic fermentation which may occur in the use of the older published methods; and the little boiling occasions a minimum solution of bodies other than starch, which could form reducing sugars. With nearly pure starch there is no occasion for use of this method. The process is valuable chiefly for estimating starch in presence of much other material which may give rise to reducing sugars by the action of acid, *e. g.*, fodders, cattle foods, and residues from starch manufacture. A sample of corn hulls, free from starch, gave only a trace of sugar by this method, but direct conversion with acid showed forty per cent. of reducing sugar.

The appended figures show the errors due to the acid method, and afford a comparison of the two:

| Material. | Moisture in sample. | Per Cent. Starch. Malt method. | Acid direct. |
|---|---|---|---|
| Starch factory feed | 10.0 | 10.0 | 40.9 |
| Impure moist starch | 12.0 | 81.3 | 82.3 |
| Impure moist starch | ... | 79.5 | 80.9 |
| Good starch | 12.8 | 84.3 | 84.6 |
| Purified dried starch | ... | 95.1 | 96.5 |
| Corn, large white kernels | 11.0 | 63.5 | 68.2 |
| Wheat, hard red variety | 10.0 | 60.5 | 65.0 |
| Bran from same wheat | 11.3 | 28.4 | 44.4 |
| Middlings from same wheat | 10.1 | 53.8 | 60.0 |
| Low flour from same wheat | 10.2 | 66.0 | 67.7 |
| Good flour from same wheat | 11.0 | 67.9 | 69.0 |
| Wheat flour | 10.0 | 70.7 | 73.6 |
| Wheat bran | 10.1 | 29.3 | 46.5 |

The method may be further improved and each chemist's needs will indicate to him useful modifications. Others may make it more perfect, and to them I commend it as the most promising method for determination of starch.

Most of the careful analytical work in the investigation of the method was done in the laboratory of the University of Nebraska, for the use of which I am indebted to the kindness of Professor H. H. Nicholson.

LABORATORY OF THE ARGO MANUFACTURING COMPANY,
NEBRASKA CITY, NEB., November 1, 1894.

## ALKALI AND SULPHUROUS ACID PROCESSES USED IN THE MANUFACTURE OF STARCH FROM CORN.

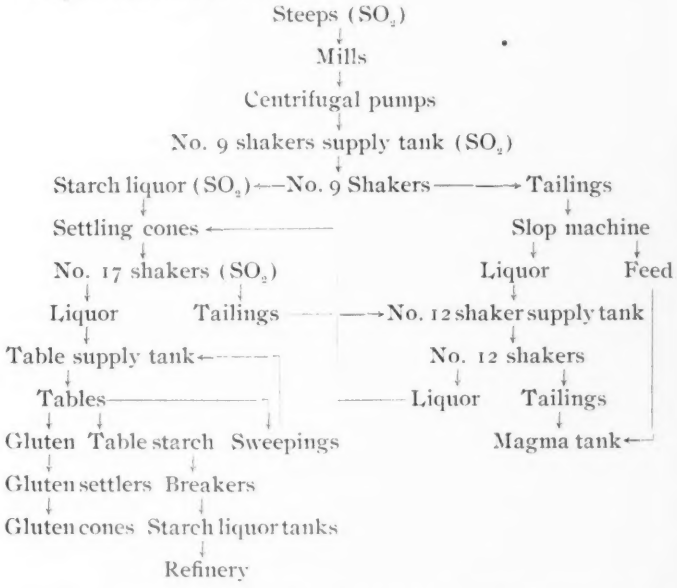
BY HORACE E. HORTON.

Received September 19, 1894.

STARCH is produced from corn at the present time by two processes, known as the alkali and sulphurous acid. I am not aware, at this moment, of the existence of any published article showing the working of these processes, and I take pleasure in presenting two outlines, showing clearly, and at a glance, their essential points.

*Alkali Process.*—

*Sulphurous Acid Process.—*




I have indicated the points at which the sulphurous acid is added, and will say in this connection, that considerable latitude is allowed. The numbers prefixed to the shakers refer to the number of the bolting cloth used.

TOPEKA, KANSAS, September 12, 1894.

## NEW BOOKS.

A TEXT-BOOK OF VOLUMETRIC ANALYSIS, WITH SPECIAL REFERENCE TO THE VOLUMETRIC PROCESSES OF THE PHARMACOPEIA OF THE UNITED STATES. DESIGNED FOR THE USE OF PHARMACISTS AND PHARMACEUTICAL STUDENTS. BY HENRY W. SCHIMPF, PH.G. pp. xviii; 400. 37 Illustrations. New York: John Wiley & Sons. 1894. Price $2.75.

This book may be considered in the light of a commentary on the Pharmacopeial assay processes. It adheres faithfully to the substance of that work but it is not a mere compilation. To the merit of the author be it said, that the numerous assay direction sprinkled throughout the Pharmacopeia are in his book

classified together systematically, which is by no means an easy task. This has been accomplished by arranging them in the first part of the book, under the following heads: Analysis by Neutralization, Precipitation, Oxidation, Indirect Oxidation (Iodometry), and Analysis of Easily Reducible Substances.

Following a general introduction, accompanied by complete directions for using apparatus, each class is introduced by a clear exposition of its principles, and in addition each assay is treated in a uniformly explicit manner. In some instances other methods are added to those official, as for example, Stolba's method to determine phosphoric acid, Personne's method for valuing potassium iodide, or Kingzett's method to determine the available oxygen in hydrogen dioxide. An excellent feature is, that with each reaction the equation and molecular weights involved are also given, the equivalent weights entering into the percentage calculation being deduced therefrom and stated.

Thus in each assay the operator finds the work a complete guide, nothing being left to conjecture or research, each subject being complete in itself, and hence Part 1st of the book becomes a systematic commentary on the assay methods of the U. S. P.

Part 2nd embraces manipulations of a more elaborate nature, such as the Assay of Opium, Cinchona, Ipecac, The Valuation of Pepsin and of the Resinous Bodies in Jalap and Scammony. These are of great value to pharmacists, and it is to be regretted that in this direction Prof. Schimpf did not enlarge upon the U. S. P. It is needless to state that in such cases gravimetric methods are employed. Attention may be called to the introduction of the methods of Benedict and Sigmundy for estimating glycerol, and of Loewenthal for tannin in barks, these being omitted in the U. S. P., and also to directions for the Volumetric Analysis of Sugar, Urine, Starch in Cereals, Alcohol, Milk, Butter, Fats in Ointments, and numerous others not mentioned in the U. S. P.

Part 3rd is devoted to Gasometric Analysis, and the estimation of Spirit of Nitrous Ether, Hydrogen Dioxide, etc., by the Nitrometer. The Appendix considers Indicators, Reagents, and Test Solutions.

This book is well illustrated and invaluable both to pharma-

cists and to chemists interested in assaying. It is an outgrowth of the Pharmacopeia and the reviewer regrets that space does not permit him to dwell at greater length on its excellent features. Every volumetric method of the Pharmacopeia is recorded explicitly with the one exception for oleic acid in which the process of Muter's Chemistry is substituted, being an improvement, however, in that the assay introduced determines oleic acid in the presence of stearic and palmitic acids which the method of the U. S. P. does not accomplish.

Notwithstanding that such a variety of subjects are embraced and condensed in a comparatively small volume, superficiality can not be charged against it. The book enables the reader, even though he has but a limited training in chemistry, to comprehend and at once carry out each assay described. It should be in the hands of every pharmacist.

J. U. LLOYD.

A TEXT-BOOK OF INORGANIC CHEMISTRY. By G. S. NEWTH, F.I.C., F.C.S. pp. xiii; 667. 146 Illustrations. London and New York: Longman's, Green & Co. 1894. Price, $1.75.

To those who have learned to appreciate the value of Newth's "Chemical Lecture Experiments," the announcement of a complete text-book by the same author, will certainly be a matter of interest. Lecturers on experimental chemistry have found the "Experiments" a most helpful guide, replete with clever, ingenious, practical devices for the lecture table, placing at the instructor's service all the latest mechanical and electrical adjuncts, and substituting for many of the antiquated illustrative features, modern striking forms of experimentation.

The same characteristics are to be encountered in the new work, freshness in material and treatment, numerous illustrations, novel and suggestive, replacing many of the time-honored wood-cuts of the standard text-book.

The author's arrangement of matter is a deviation from all the customary methods. He divides his work into three quite distinct parts. Part I—"Introductory Outlines." 150 pages are devoted to theory and chemical physics, notation, nomenclature, atomic weights, valence, heat, pressure, electrolysis, solutions, thermo-chemistry, periodicity, etc. This whole section is

marked by great clearness of presentation and accuracy of statement.

Part II. "The Study of Four Typical Elements." 150 pages are devoted to quite an exhaustive treatment of hydrogen, oxygen, nitrogen, and carbon, with their more important compounds. This section unfrequently recalls Hofmann's famous "Einleitung" where likewise a few elements are utilized to bring out the main essentials of chemical fact and theory. Especially noteworthy in this part is the admirable treatment of *flame* and *combustion* thoroughly up to the times, and far in advance of any existing text-book treatment of these important topics.

Part III. 350 pages are devoted to the remainder of the elements, following closely the periodic classification. The space given each element is necessarily somewhat limited, sodium, for example, receiving but twelve pages, magnesium, four pages, etc. Here we notice, however, as a rule, that the work is well up to the times, notably in technical manufacturing processes. Geographical reference is almost entirely omitted, with some rare exceptions, as in the case of mercury.

Just what is the most advantageous arrangement of the matter in a text-book of this size, is a moot question. Among recent works we find on the one hand Mixter's, adhering rigidly to the periodic classification, and on the other hand Freer's, following the same classification after a study of oxygen, Remsen's doing likewise after a study of oxygen, hydrogen, and chlorine, while, as we have seen, Newth prefaces the same classification with a study of four elements, and prefaces the latter also with an extended section on theoretical and physical chemistry. From my own experience and observation I am inclined to the opinion that the brighter, more persevering students in a college class make satisfactory progress with any of these types, while, on the contrary, a considerable number can profitably take up such a text-book as Newth's only after preliminary drill in some one of the excellent elementary works introducing theoretical concepts gradually, with the acquisition of the necessary experimental facts.

While recognizing fully the many excellent qualities in Dr. Newth's work, attention should be called to several of those

deficiencies which are almost inevitable in an author's first edition. Thus while there is an excellent chapter on thermochemistry in the introduction the subject is almost entirely ignored in the treatment of individual elements and compounds, although in so many cases (as in that of the allotropic forms of phosphorus) it serves admirably to explain important facts.

Uniformity and simplicity in nomenclature are frequently neglected. Note, for example, the following two headings of sections within a few pages of each other: (1) *Arsenuretted Hydrogen* (*Arsenic Trihydride*, *Arsine*), and (2) *Antimony Hydride* (*Antimoniuretted Hydrogen*).

The space assigned individual metals seems frequently too brief; and despite the author's excuse in the preface, I can not approve of the very step-motherly treatment in a book of nearly 700 pages, of the so-called rare metals. Titanium, which is so important to the metallurgist and which forms a larger percentage of our planet than does carbon, receives four lines. Zirconium, cerium, and thorium are passed by with the same meager mention, although their oxides are now in every-day use in our homes for illuminating purposes. This latter fact is omitted entirely, while mention is made of the now much less extended employment of lime for similar purposes. Tungsten, molybdenum, and uranium receive together but one page.

While, as already stated, the work in most instances is quite up to the times—for example, in the account of the lately discovered new element in the atmosphere—still in certain cases there is an inexcusable lack of recognition of recent fact and method.

Thus, under aluminum, we find but a single method of preparing the metal. The historically interesting process of St. Clair Deville receives over a page of description. But not a gram of aluminum is made to-day by that method. That more and more valuable servant of the modern chemist, electrolysis, is granted in fact but scant attention. While a brief allusion to the action of the current on sodium chloride is found in the preface, no mention is made of the important reaction in connection with either chlorine or with sodium compounds. Similarly, while fourteen different methods for preparing oxygen are described in detail, not a word is given to the simplest and most

elegant of all, the reaction between water and sodium peroxide, now employed in every laboratory and lecture-room. No mention is to be found of red fuming nitric acid.

The date of 1876 for Moissan's discovery of free fluorine is probably a typographical error. T. H. NORTON.

DIE MASCHINELLEN HILFSMITTEL DER CHEMISCHEN TECHNIK. von Alwin Parnicke. pp. 320. 327 Illustrations. H. Bechhold, Frankfort, A. M. 1894.

The lack of a good manual on the methods used for the mechanical preparation of substances used in the chemical industries to which Mr. Pemberton has already called attention in these columns, (see this JOURNAL, *1893*, p. 634) is supplied in the excellent digest of the subject contained in this book. The sections into which the book is divided may be translated as follows: 1. Sources of Power. 2. Transmission of Power. 3. Methods of Transportation. 4. Grinding. 5. Mixing. 6. Melting, Dissolving, and Extraction. 7. Concentration. 8. Mechanical Separation. 9. Drying. 10. Weighing, Determination of Temperature, Pressure, and Draught. 11. Laws Relating to the Subject.

The book is well printed and the illustrations are excellent, an important matter in such a book. It is to be hoped the book may find a translator who will condense it sufficiently for class use. E. H.

THE ELEMENTARY NATURE OF CHLORINE. BY HUMPHRY DAVY, SEC. R. S., 1809–1818. PAPERS PUBLISHED IN THE PHILOSOPHICAL TRANSACTIONS. ALEMBIC CLUB REPRINTS, No. 9. 80 pp. Edinburgh: William F. Clay. 1894.

This reprint is no less interesting than its predecessors. The first three papers give the results of experiments made to determine the properties and composition of "muriatic acid." In the remaining six papers Davy describes a few experiments by other chemists and many of his own upon "oxymuriatic acid," discusses them and, without asserting that this gas is an element, suggests that it be called chlorine, on account of its color and because it "is not known to contain oxygen and can not contain muriatic acid." A short account of the discovery and properties of "Euchlorine" is found in one of the papers.

L. B. HALL.